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The objectives of this task were the evaluation of the available basis for the prediction of destruction efficiencies of hazardous wastes in large commercial incinerators and for scaling incinerators to much larger sizes.

A review of major commercial facilities and of waste-facilities matching criteria led to the selection of the four incinerator types having the widest applicability for waste destruction. These were the liquid injection, the fluidized bed, the multiple hearth and the rotary kiln incinerators.

Any prediction of the hazardous components destruction efficiency relies on the knowledge of the temperature/residence time requirements needed for complete thermal decomposition. These requirements may be influenced by the oxygen concentration during the process of decomposition. In Section 4.1 a method utilizing computerized thermal equilibrium computations and kinetic considerations is described. Intermediate, potentially hazardous species, can be detected and the necessary laboratory decomposition/combustion experiments pinpointed.

Recommended steps for the development of a hazardous waste incinerator scale-up methodology conclude this report.

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HAZARDOUS MATERIAL INCINERATOR DESIGN CRITERIA

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report "Hazardous Material Incinerator Design Criteria" is the first step of a major effort to reduce pollution of our environment by improperly disposed solid waste. Recent events have shown that serious problems are associated with traditional waste disposal methods. In order to implement alternative ways of disposing of industrial wastes, such as high efficiency incineration, more has to be known about them. The program this study is part of is intended to take the field of hazardous waste incineration out of the category of an art and make it more of a science--to increase its efficiency and decrease cost and energy usage. Further information may be obtained from the Organic Chemicals and Products Branch.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

The objectives of this task were the evaluation of the available basis for the prediction of destruction efficiencies of hazardous wastes in large commercial incinerators and for scaling incinerators to much larger sizes.

A review of major commercial facilities and of waste-facilities matching criteria led to the selection of the four incinerator types having the widest applicability for waste destruction. These were the liquid injection, the fluidized bed, the multiple hearth and the rotary kiln incinerators.

Of these four devices, the liquid injection incinerator enjoys the most abundant analytical and experimental research and development background. Though no complete and coherant method for the prediction of specific emissions levels exists, possible approaches to such predictions are available. Scale-up is still an uncertain art. However, the art and science of modeling are progressing and may provide better means for emissions prediction/control and for scale-up in the not too distant future. The liquid injection incinerator is discussed in Section 3.2.

Fluidized bed incinerators are the newest arrival in the field of incineration. The intensive development efforts expended to develop clean coal combustion and coal derived clean fuels technologies will surely provide some very valuable insights into the waste incineration phenomena. There are as yet no reliable methods for emissions prediction or scale-up, but an analytical base is in the process of development and applicable data is becoming more abundant. Section 3.3 is devoted to the field of fluidized bed development.

Multiple hearth incinerators are widely used, but not much analytical background was found in the literature. The reasons may well include the difficulties in analyzing the fundamental mechanisms in this device where the vapors, combustion gases and solids all follow singularly contorted paths. See Section 3.4 for a description of fluid and solids flows and of an experimental method to evaluate solids mixing.

The rotary kiln incinerator is probably the most widely applicable device since it can handle solids, liquids and sludges (even explosives). Mathematical treatment of the heat flow to the charge appears possible, as discussed in Section 3.5. However, information on the mixing in the solids charge and heat transfer between the charge, the walls and the combustion gases is lacking and will have to be acquired by appropriate measurements in the field.

Any prediction of the hazardous components destruction efficiency relies on the knowledge of the temperature/residence time requirements needed for complete thermal decomposition. These requirements may be influenced by the oxygen concentration during the process of decomposition. In Section 4.1 a method utilizing computerized thermal equilibrium computations and kinetic considerations is described. Intermediate, potentially hazardous species, can be detected and the necessary laboratory decomposition/combustion experiments pinpointed.

A listing of recommended steps for the development of a hazardous waste incineration methodology conclude this report.

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SECTION 1

INTRODUCTION

At the present state-of-the-art, incineration or other thermal techniques appear to be the most likely method available for the large-scale destruction of hazardous organic wastes. The problem often encountered in its application, especially by a Regulatory Agency, is how one determines safety in a new situation. For example, if a given waste is safely incinerated in a small pilot scale incinerator, how does one determine whether a larger, supposedly similar unit is capable of achieving the same degree of destruction. This problem translates into the establishment of scale-up criteria for incinerators.

The development and verification of such criteria would have many benefits beyond the above-mentioned one. Currently, it is necessary to conduct expensive large scale tests prior to establishing the safety of an incineration procedure. Scale-up criteria would permit these tests to be performed on smaller units with a resultant decrease in cost and at a much greater level of safety. Such criteria could also be useful in attempts to reduce fuel usages in an incinerator.

Task 5006 was initiated on January 4, 1978 under EPA Contract 68-03-2500 as a first step in addressing these needs. Conceptually, the Task was intended to examine the experimental and analytical tools available for the characterization of wastes and incineration devices and recommend which may best lend themselves to determining usable scale-up criteria. The contractor was instructed to consider theoretical approaches such as detailed flame modeling only as a tool to the establishment of such criteria not as an end-point to the research. Techniques such as dimensional analysis were to be examined and recommendations as to their potential for further research to be made. The task objectives, formulated to support this goal, were to evaluate the available bases for predicting the destruction efficiency of hazardous wastes in the four most widely used types of incineration devices and for scaling these to much larger sizes.

The approach taken included the examination of commercial incineration installations and of the literature pertaining to the combustion of liquids, solids and sludges in general, and to the incineration mechanisms encountered in four of the most widely used incinerators in particular. The dichotomy between the methods used to design commercial incinerators and the methods for investigating combustion and flow phenomena is readily apparent. Commercial incinerators are by and large designed on the basis of past designs and rely heavily on the talents and experience of the designers. The efforts of the scientists and engineers interested in incineration are, by contrast, directed towards uncovering the universal laws controlling incineration and have therefore a limited capability to deal with the EPA's specific requirements. This study examines the "middle ground" between these.

In this report, Section 2 is a survey of commercial incineration facilities; Section 3 characterizes four major types of incinerators - liquid injection, fluidized bed, rotary kiln and multiple hearth; Section 4 discusses how the thermochemical properties of the wastes ~~involved~~ affect their incineration and how the application of thermochemical analysis of the wastes can be used; Section 5 recommends what areas should be explored by further research into the development of incineration scale-up criteria.

SECTION 2

COMMERCIAL INCINERATORS SURVEY

2.1 INTRODUCTION

In the course of prior studies[1] pertaining to thermal destruction of hazardous wastes, TRW has identified a large number of wastes generated by various industries, and identified wastes which could be incinerated. A systematic classification of wastes and of existing commercial incinerator installations was undertaken and a matching of wastes and incinerator types worked out. As a result of that work 50 candidate wastes have been assigned to 14 facilities. Based on this work we have selected four types of incinerators and examined the present state of knowledge of the combustion in these incinerators. A brief summary of the incineration facilities survey and of the waste-incinerator matching effort, followed by a brief description of the selected incinerator types is given in this section.

2.2 INCINERATOR TYPES

The survey of commercial incineration installations showed that the eight types of incinerators most commonly used were

- Liquid injection incineration
- Fluidized bed incineration
- Multiple hearth incineration
- Rotary kiln incineration
- Catalytic combustion
- Molten salt pyrolysis/combustion
- Pyrolysis
- Wet oxidation

We selected for our study, the first four of that list, the most versatile at accepting a wide variety of wastes.

2.3 WASTE-INCINERATION FACILITY MATCHING CRITERIA

In matching different wastes with commercial incineration facilities, the physical form (solid, liquid, etc.) of the wastes are more important than the chemical properties. The most important chemical characteristics are the chlorine and sodium contents of the wastes. Wastes containing a large concentration of halogens can overload the scrubbing equipment on certain incinerators or require the use of a highly hydrogenated auxiliary fuel, so that HCl, not Cl_2, is liberated. Sludges containing substantial amounts of sodium can cause defluidization of fluidized beds by forming low melting eutectic mixtures (such as NACl - Na_2CO_3 or NaCl - Na_2SO_4)[2]. Furthermore, if the particles of the fluidized bed are silica-sand, Na_2SO_4 will react with the silica to form a viscous sodium-silicate glass, which will cause rapid defluidization.

The criteria used for matching different wastes to the various incineration facilities are:

1) Physical form:
   Gas, liquid, slurry, sludge, or solid

2) Temperature range required for destruction:

   a) >1360 K (2000 F)
   b) 1030-1360 K (1400-2000 F)
   c) 640 -1030 K (700-1400 F)
   d) <640 K (700 F)

3) Off-Gases:

   a) Essentially oxides of carbon and nitrogen, and water vapor

   b) Halogen, sulfur, phosphorus, or volatile metal species

4) Ash:

   Nonfusible, fusible, or metallic

5) Heating Value:

   a) >23 MJ/Kg (10,000 Btu/lb)
   b) 12-23 MJ/Kg (5,000-10,000 Btu/lb)
   c) <12 MJ/Kg (5,000 Btu/lb)

Additions to these criteria may become necessary when the list of hazardous wastes is increased in the future.

A detailed description of each of the four selected incinerators will be found in the section on commercial incinerator facilities (Section 2.5).

2.4 APPLICABILITY OF THE FOUR SELECTED INCINERATORS

Liquid injection, fluidized bed, multiple hearth, and rotary kiln incinerators are all widely used to dispose of hazardous wastes. A particular incinerator may be better suited for incineration of a particular type of waste based on the physical characteristics of the waste. Solids, sludges, and slurries of high viscosity liquids can be disposed in rotary kiln, fluidized bed, or multiple hearth incinerators, but not in a liquid injection incinerator. If the ash resulting from incineration of a waste is fusible, multiple hearth or fluidized bed incinerators are not well suited for its disposal. Furthermore, the multiple hearth and fluidized bed incinerators are not capable of operating at elevated temperatures - so that if a temperature over 1360 K (2000 F) is needed for destruction, only rotary kiln or liquid injection incinerators are acceptable. A matrix for matching wastes and facilities is shown in Figure 1.

In the TRW report, "Destructing Chemical Wastes in Commercial Scale Incinerators"[3], fifty wastes are prioritized on the basis of the degree of their hazard, and the amount produced annually. Eight different incinerators (liquid injection, fluidized beds, multiple hearth, rotary kiln, wet air oxidation, catalytic/thermal, pyrolysis, and molten salt incinerators) were studied as to their applicability in destroying the prioritized wastes in prior work. A test plan was developed and commercial facilities incorporating these incinerators tested[4-11]. It was concluded that the liquid injection, rotary kiln, and fluidized bed incinerators had widespread applicability, whereas the multiple hearth incinerator had moderate applicability. The liquid injection and fluidized bed offer excellent mixing so that all vaporized waste can be effectively destroyed. The rotary kiln and multiple hearth incinerators utilize mechanical mixing, permitting the solid or liquid wastes to be exposed to hot oxidizing gas for as long as needed for their destruction. These incinerators are particularly well suited for the destruction of solids and highly viscous sludges.

		FACILITY TYPE			
WASTE CHARACTERISTICS		LIQUID INJECTION	MULTIPLE HEARTH	ROTARY KILN	FLUIDIZED BED
GAS			▨ *		
LIQUID	LOW VISCOSITY (BELOW 500 SSU) **		▨		
	HIGH VISCOSITY (ABOVE 500 SSU)	▨	▨		
SLURRY	LOW VISCOSITY (BELOW 500 SSU)		▨		
	HIGH VISCOSITY (ABOVE 500 SSU)	▨	▨		
SLUDGE		▨			
SOLID	FRIABLE POWDER	▨			
	TARRY	▨	▨		▨
TEMP. RANGE FOR DESTRUCTION	1370°K		▨		▨
	1030-1370°K				
	640-1030°K	▨	▨	▨	▨
	640°K	▨	▨	▨	▨
ASH	NON FUSIBLE				
	FUSIBLE		▨		▨
	METALLIC				

* ▨ NOT APPLICABLE

** 500 SSU = 0.00011 M^2/S

Figure 1. Waste and facilities matrix.

2.5 COMMERCIAL INCINERATOR FACILITIES

2.5.1 Liquid Waste Combustors

Liquid waste combustors are versatile units which can be used to dispose of virtually any combustible liquid waste with a viscosity less than 2.2×10^{-3} m^2/s (10,000 SSU). There are a wide variety of liquid waste combustors presently marketed throughout the manufacturing industries[12].

Operation Principle--

Before a liquid waste can be combusted, it must be converted to the gaseous state. This change from a liquid to a gas occurs inside the combustion chamber and requires heat transfer from the hot combustion product gases to the injected liquid. In order to effect a rapid vaporization (i.e., increase heat transfer), it is necessary to increase the exposed liquid surface area. Most commonly the amount of surface exposed to heat is increased by finely atomizing the liquid to small droplets, usually to a 40 m size or smaller. This atomization can be achieved mechanically, by two phase flow, or by a combination of both methods. It is usually achieved in the liquid burner directly at the point of fuel and air mixing.

Atomization is the heart of any good liquid incinerator. Mechanical means of atomization include rotary cup and pressure atomization. The rotary cup consists of an open cup mounted on a hollow shaft. The cup is spun rapidly and liquid admitted through the hollow shaft. A thin film of the liquid to be atomized is centrifugally torn from the lip of the cup and surface tension reforms it into droplets. To achieve conical shaped flames an annular high velocity jet of air (primary air) must be directed axially around the cup. If too little primary air is admitted the fuel will impinge on the sides of the incinerator. If too much primary air is admitted the flame will not be stable, and will be blown off the cup. For fixed firing rates, the proper adjustment can be found and the unit operated long periods of time without cleaning.

Pressure atomizing may take many forms. The familiar garden hose nozzle is one example. Most commonly the liquid is given a direction by internal tangential guide slots to the center of the nozzle and then released axially through an orifice. Good atomization can be achieved at moderate pressures

0.68 MPa to 1.0 MPa (100 to 150 psi). Disadvantages include a limited variable flow range at low pressures and, especially in the smaller sizes, a tendency to plug with foreign matter. Large sizes are reasonably free from this problem.

Liquid burners require considerably more turbulence and time to complete combustion than do gas burners. To complete combustion good mixing of the liquid spray and air is needed, and the larger the particle, the greater distance they will go before being completely vaporized and burned. Forced draft units, if well designed, will result in higher air velocities and therefore will have better combustion characteristics than natural draft units. Burners must be located to prevent flame impingement on walls and, in the case of multi-burner units, interference with one another. While multiple atomizers can be located within a single air register, the performance will suffer, and combustion volume must be added to offset this characteristic. Whenever possible, the number of liquid streams should be minimized.

Liquid streams can carry impurities of every sort. Futhermore, they may be highly viscous, which makes handling and atomizing difficult. Liquids should generally have a viscosity of 2.2×10^{-3} m^2/s (10,000 SSU) or less to be satisfactorily pumped and handled in pipes. For atomization, they should have a maximum viscosity of 1.6×10^{-4} m^2/s (750 SSU). If the viscosity exceeds this value the atomization may not be fine enough, and the resultant droplets of unburned liquid may cause smoke or other unburned particles to leave the unit. Viscosity can usually be controlled by heating with tank coils or in-line heaters. Should gases be evolved in any quantity before the desired viscosity is reached, they may cause unstable fuel feed and burning. If this occurs, the gases should be trapped and vented safely, either to the incinerator or elsewhere. If preheating is not feasible, a lower viscosity and miscible liquid may be added to reduce the viscosity of the mixture.

Prior to heating a liquid waste stream, a check should be made to insure that undesirable preliminary chemical reactions such as polymerization, nitration, oxidation, etc., will not occur. Should these occur, it may be more desirable to fill disposable containers with the liquid and treat them as solids. Other preparatory steps may include filtration, degassing, pressurizing, neutralizing, storage, mixing, etc. In every one of these steps care must be employed to see that undesired and harmful results do not occur. Pump and piping materials of construction must be suitable for the liquids encountered. Liquids that can solidify or become too viscous should have jacketed or traced piping. Provision should be made to clean out the piping and equipment when long shutdowns occur. This is usually done by purging with steam. Certain atomizing nozzles should always be blown clear with steam whenever flow is stopped. If not, the residual heat in the incinerator may cause thermal cracking of the liquid remaining in the nozzles, resulting in partial or complete pluggage.

Process Design--

Liquid waste incinerators can be vertically or horizontally fired units. Their operating temperatures range from 920 K (1200 F) to 1920 K (3000 F) (most units operate around 1140 K (1600 F) and residence times range from one half to two seconds. Most units have combustion chamber volumes which provide for a heat release of approximately 0.25 MW/m^3 (25,000 $Btu/hr\text{-}ft^3$), however, the vortex type liquid combustor has an unusually high heat release of about 1.0 MW/m^3 (100,000 $Btu/hr\text{-}ft^3$).

A typical horizontally fired liquid waste incineration system is presented (Figure 2). This particular system is the one operated by the Dow Chemical Company at their Midland, Michigan facility. The unit is a 24 MW (81 million Btu/hr) incinerator which has a combustion chamber 10.6 m (35 ft.) long and 0.93 m^2 (10 ft^2) in cross section. Wastes are fed to the unit through a combination of four dual-fired nozzles. Combustion gases are quenched in a spray chamber, followed by a high-pressure-drop venturi scrubber, and a cooler/mist-eliminator. About 6.3×10^{-2} m^3/s (1000 gpm) of water is recycled from the primary tanks to the wastewater treatment facilities to furnish scrubbing water. This water flows back to the wastewater plant for treatment. About 1,100 hp. is required for this unit.

The majority of the liquid wastes treated in the Dow unit are solids at room temperature and must be kept hot in order to remain liquid. Many residues are chlorinated and can contain as high as 50 percent chlorine, plus several percent of ash in the form of ash in the form of Fe, Ca, Mg, Na, oxides and chlorides.

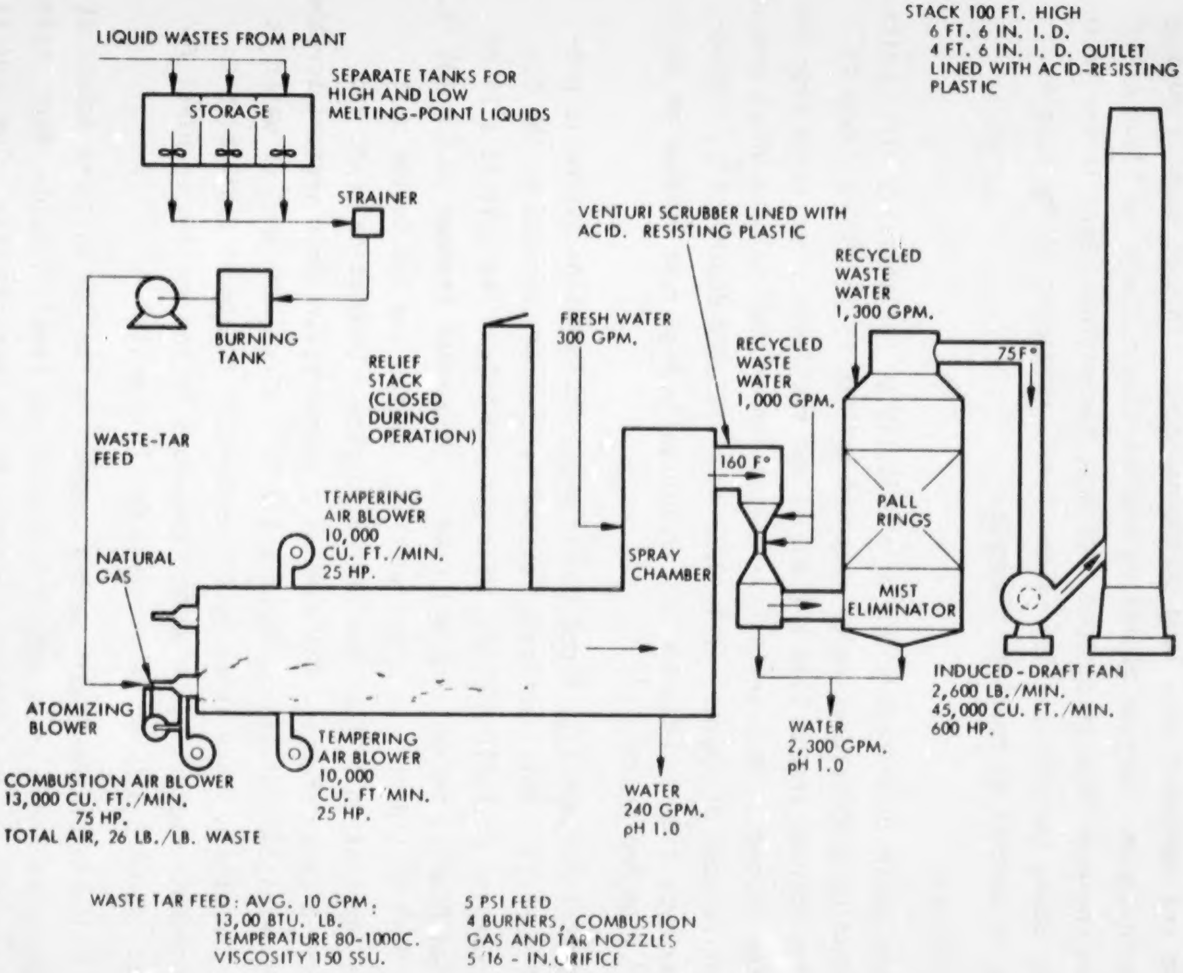
LIQUID WASTES FROM PLANT
STORAGE
SEPARATE TANKS FOR HIGH AND LOW MELTING-POINT LIQUIDS
STRAINER
BURNING TANK
WASTE-TAR FEED
NATURAL GAS
ATOMIZING BLOWER
COMBUSTION AIR BLOWER 13,000 CU. FT./MIN. 75 HP.
TOTAL AIR, 26 LB./LB. WASTE
TEMPERING AIR BLOWER 10,000 CU. FT./MIN. 25 HP.
TEMPERING AIR BLOWER 10,000 CU. FT /MIN. 25 HP.
RELIEF STACK (CLOSED DURING OPERATION)
FRESH WATER 300 GPM.
SPRAY CHAMBER
WATER 240 GPM. pH 1.0
VENTURI SCRUBBER LINED WITH ACID. RESISTING PLASTIC
160 F°
RECYCLED WASTE WATER 1,000 GPM.
RECYCLED WASTE WATER 1,300 GPM.
PALL RINGS
MIST ELIMINATOR
WATER 2,300 GPM. pH 1.0
75F°
INDUCED - DRAFT FAN 2,600 LB./MIN. 45,000 CU. FT./MIN. 600 HP.
STACK 100 FT. HIGH
6 FT. 6 IN. I. D.
4 FT. 6 IN. I. D. OUTLET
LINED WITH ACID-RESISTING PLASTIC
WASTE TAR FEED: AVG. 10 GPM.
13,00 BTU. LB.
TEMPERATURE 80-1000C.
VISCOSITY 150 SSU.
5 PSI FEED
4 BURNERS, COMBUSTION
GAS AND TAR NOZZLES
5 16 - IN. ORIFICE

Figure 2. Horizontally fired liquid waste incineration system. (English systems of units in the actual commercial incineration system).

A typical vertically fired liquid waste incinerator is presented (Figure 3). This particular unit is designed and marketed by the Prenco Division of Pickands Mather and Company. It is claimed to be a versatile system in that it can be brought up to operating temperature in one to two hours with minimal fuel requirements. This quick warm-up permits periodic rather than continual operation.

The Prenco vertical combustor operates in the following manner. A mixture of auxiliary fuel (usually natural gas) and high pressure air are first fed into the vertical retort to bring it up to proper waste decomposition temperature. When the retort reaches the correct temperature, as determined by the temperature measuring instruments, fuel flow is modulated and waste is admitted to the air-waste entrainment compartment. From there the aerated waste is fed into a turbulence compartment where it is mixed with more high pressure air and injected into the high-temperature vertical retort. Here the process breaks down the waste by molecular dissociation, oxidation, and ionization. The gases and any inert particles produced flow vertically through the air cone and out of the top of the retort.

Decomposition efficiency is greatly increased through the injection of pressurized air at a point near the top of the retort through ports in a specially designed refractory module. The air cone, which serves as a fuel saver, increases decomposition efficiency by increasing heat retention. It also provides additional air for an afterburner effect. In addition the air cone reduces the temperature of the decomposed effluent to about 620 K (650 F). As a result, scrubbers and effluent test equipment can be utilized if desired.

The Prenco unit utilizes air preheat. Intake of air from the top of the upper nacelle causes it to be preheated as it travels down the outer wall of the decomposition chamber to both the turbo-blower and afterburner fans. The use of preheated air significantly increases decomposition efficiency and economy of operation.

Process Applicability--

Liquid waste incinerators are generally applicable to the ultimate disposal of most forms (including dilute) of combustible liquid waste materials

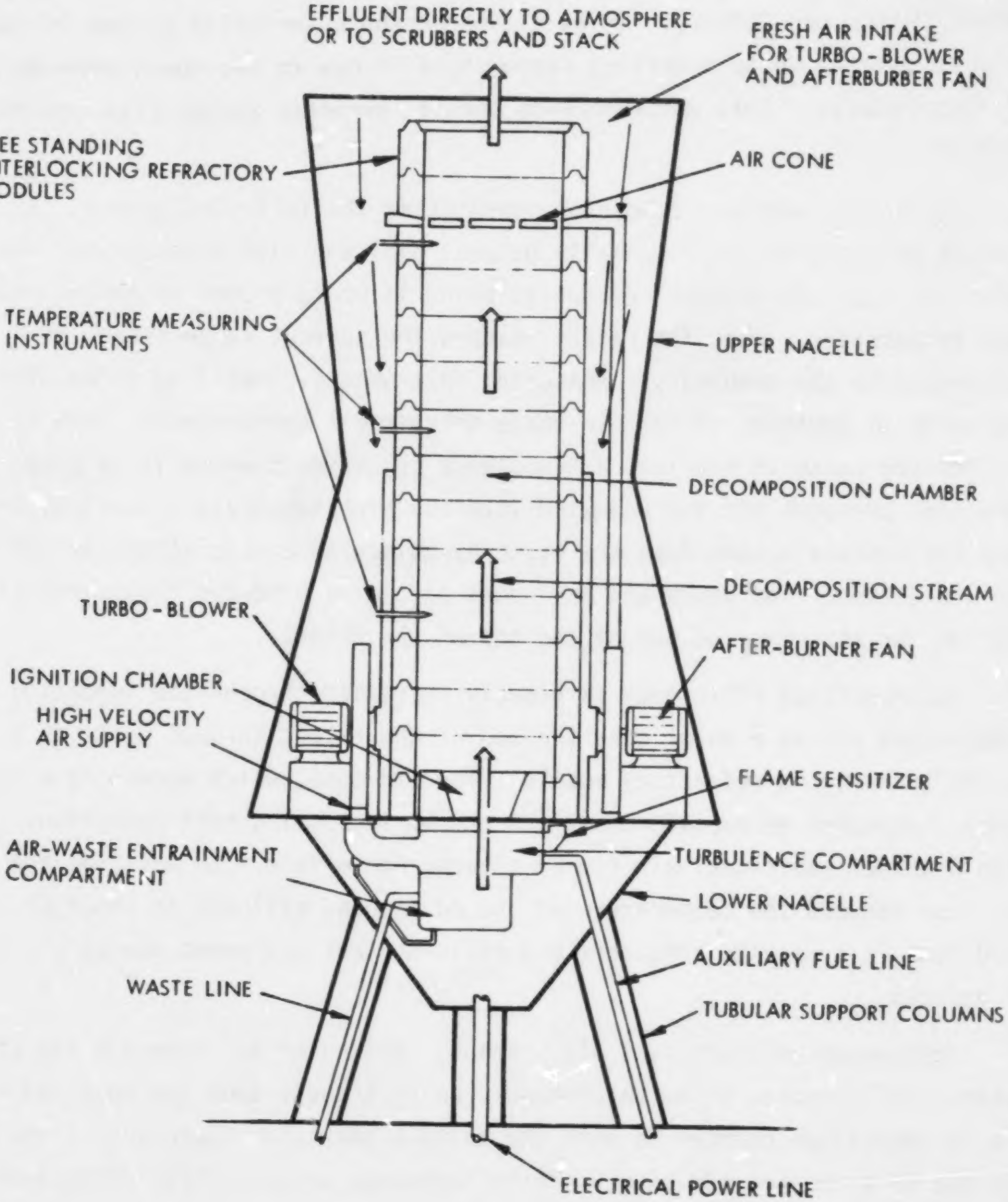
EFFLUENT DIRECTLY TO ATMOSPHERE OR TO SCRUBBERS AND STACK
FRESH AIR INTAKE FOR TURBO - BLOWER AND AFTERBURBER FAN
FREE STANDING INTERLOCKING REFRACTORY MODULES
AIR CONE
TEMPERATURE MEASURING INSTRUMENTS
UPPER NACELLE
DECOMPOSITION CHAMBER
DECOMPOSITION STREAM
TURBO - BLOWER
AFTER-BURNER FAN
IGNITION CHAMBER
HIGH VELOCITY AIR SUPPLY
FLAME SENSITIZER
AIR-WASTE ENTRAINMENT COMPARTMENT
TURBULENCE COMPARTMENT
LOWER NACELLE
AUXILIARY FUEL LINE
WASTE LINE
TUBULAR SUPPORT COLUMNS
ELECTRICAL POWER LINE

Figure 3. Typical vertically fired liquid waste incinerator.

and represent proven technology. Some of the materials currently being disposed with this type incinerator are presented (Table 1).

2.5.2 Fluidized Bed Incineration

Fluidized bed incinerators are versatile devices which can be used to dispose of solid, liquid and gaseous combustible wastes. The technique is a relatively new method for ultimate disposal of waste materials. It was first used commercially in the United States in 1962 and has found limited use in the petroleum industry, paper industry and for processing nuclear wastes. In addition, fluidized bed combustion has been applied for the disposal of sanitary sludge[12].

Operating Principle--

A typical fluidized bed incinerator is shown schematically (Figure 4). Air driven by a blower enters a plenum at the bottom of the combustor and rises vertically through a distributor plate into a vessel containing a bed of inert granular particles. Sand is typically used as the bed material. The upward flow of air through the sand bed results in a dense turbulent mass which behaves in a way that is similar to that of an air flow through a liquid. Waste material to be incinerated is injected into the bed and combustion occurs within the bubbling bed.

Air passage through the bed produces strong agitation of the bed particles. This promotes rapid and relatively uniform mixing of the injected waste material within the fluidized bed.

The mass of the fluidized bed is large in relation to the injected material. Bed temperatures are quite uniform and typically in the 1030 to 1140 K (1400 to 1600 F) range. At these temperatures, heat content of the fluidized bed is approximately 600 MJ/m^3 (16,000 Btu/ft^3) thus providing a large heat reservoir. By comparison, the heat capacity of flue gases at similar temperatures is three orders of magnitude less than a fluidized sand bed.

Heat is transferred from the bed into the injected waste materials to be incinerated. Upon reaching ignition temperature (which takes place rapidly) the material combusts and transfers heat back into the bed. Continued bed agitation by the fluidizing air allows larger waste particles to remain

TABLE 1. LIQUID WASTES CURRENTLY BURNED IN LIQUID WASTE INCINERATION

Separator sludges
Skimmer refuse
Oily waste
Detergent sludges
Digester sludges
Cutting oils
Coolants
Strippers
Phenols
Wine wastes
Potato starch
Vegetable oils
Washer liquids
Still & reactor bottoms
Soap & detergent cleaners
Animal oils & rendering fats
Cyanide & chrome plating wastes
Lube oils
Soluble oils
Polyester paint
PVC paint
Latex paint
Thinners
Solvents
Polymers
Resins
Cheese wastes
Dyes
Inks

Off-specification isoprene
Hexachlorocyclopentadiene
Organophosphate pesticides
Waste from polymer polyol production
Dodecyl mercaptan wastes
Fluorinated herbicide wastes
Ethylene glycol manufacture residue
Waste residues from alkyl benzene production

Perchloroethylene manufacture still bottoms

Alkyl and oryl sulfonic acid wastes
Still bottom from acetaldehyde production.

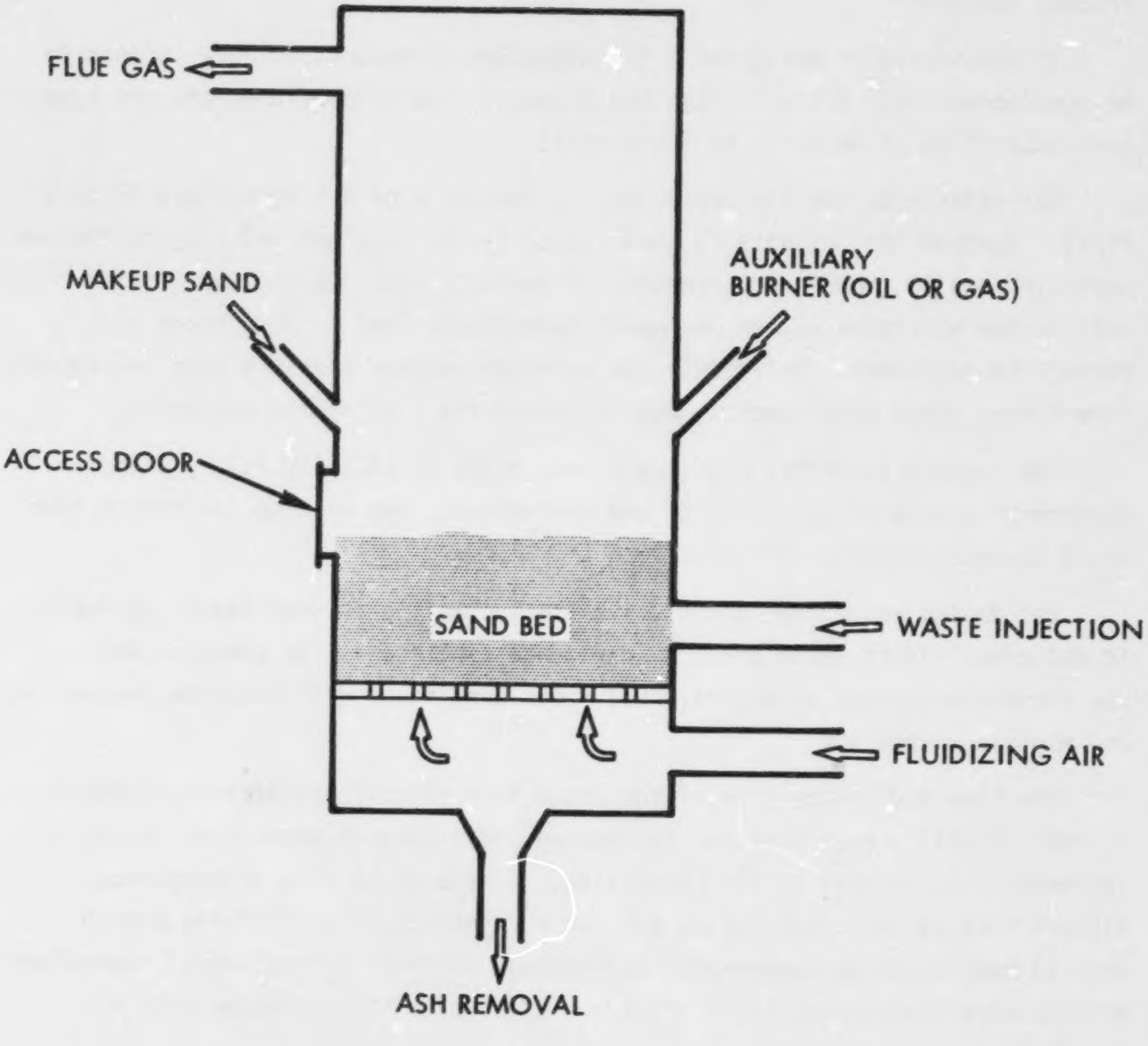
FLUE GAS
MAKEUP SAND
AUXILIARY BURNER (OIL OR GAS)
ACCESS DOOR
SAND BED
WASTE INJECTION
FLUIDIZING AIR
ASH REMOVAL

Figure 4. Schematic of a fluidized bed combustor.

suspended until combustion is completed. Elutriated fines are carried off the bed by the exhausting flue gases at the top of the combustor. These gases are subsequently processed and/or scrubbed before atmospheric discharge.

Process Design--

In specifying or designing a fluidized bed combustor, primary factors to be considered are: gas velocity; bed diameter; bed temperature; and the type and composition of waste to be incinerated.

Gas velocities are typically low, in the order of 1.5 to 2.4 m/s (5 to 8 ft/s). Maximum gas velocity is constrained by the terminal velocity of the bed particles and is therefore a function of particle size. Higher velocities result in bed attrition and an increased particulate load on downstream air correction equipment. Relatively low velocity reduces pressure drop and therefore lowers power requirements, but increases the size of the equipment.

The largest fluidized beds are on the order of 15 m (50 ft) in diameter. At nominal values of gas velocity and temperature, the maximum volumetric flow would be approximately 1200 m^3/s (2.5×10^6 acfm).

Bed depths range from about 0.4 m (16 inches) to several feet. Variations in bed depth affect waste particle residence time and system pressure drop. One therefore desires to minimize bed depth consistant with complete combustion and minimum excess air.

The type and composition of the waste is a significant design parameter in that it will impact storage, processing and transport operations (prior to incineration), as well as the combustion. If the waste is a heterogeneous mixture such as municipal refuse and has a relatively low <19 MJ/kg (<8000 Btu/lb) heating value, processing (shredding, sorting, drying, etc.) operations will be more complex and auxiliary fuel addition to the combustor will be required.

Process Applicability--

Many of the fluidized bed incineration applications involve the disposal of sludges or slurried wastes. This may necessitate a dewatering step in processing the water prior to incineration if combustion gases are to be used for steam-electric or gas turbine power generation. If power generation is a desired by-product of the incineration process, then waste moisture content values less than approximately 60 percent are required. Moisture values in excess of this value, or heavy concentrations of inert matter will require auxiliary fuel burners to preheat the waste and ensure sufficient heat content in the flue gases. Pre-drying of the sludge may be accomplished by aeration or more sophisticated mechanical systems involving the addition of heat. Table 2 shows a list of wastes currently incinerated in fluidized bed facilities.

Waste material is pneumatically, mechanically or gravity fed into the fluidized bed. Normally, inhomogeneous waste material must be reduced in size (shredded, pulverized, etc.) to facilitate the feed system operation and permit injection, distribution and combustion within the fluidized bed.

Advantages

1) The combustor design concept is simple and does not require moving parts in the elevated temperature regions of combustion.
2) Designs are compact due to high volumetric heating rates 1.0 MW/m^3 to 2.0 MW/m^3 (100,000 to 200,000 Btu/hr-ft^3) resulting in lower capital investment.
3) Comparatively low gas temperatures and excess air requirements* minimize formation of nitric oxide and the cost of equipment.

Limitations

1) Bed diameters are limited with present design technology; therefore, maximum volumetric flow rates per unit are limited.
2) Removal of inert residual material from the bed is a potential problem area.

2.5.3 Multiple Hearth Incinerators

The multiple hearth incinerator (commonly called a Herreshoff furnace) is a versalite unit which has been utilized to dispose of sewage, sludges, tars, solids, gases, and liquid combustible wastes. This type of unit was initially designed to incinerate sewage plant sludges in 1934. In 1968, there were over 125 installations in operation with a total capacity of

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*For example, excess air requirements as low as 5 percent have been reported in the combustion of coal in fluidized bed reactors. Low excess air requirements reduce the size and cost of gas handling equipment.

TABLE 2. WASTES CURRENTLY INCINERATED IN FLUIDIZED BEDS

Off-specification phenol
Amiben manufacture liquid wastes
Corboryl manufacture waste
Ethylene manufacturing wastes
Waste from toluene diamine production from dinitrotoluene
Tetraethyl orthosilicate wastes
Organic wastes from pharmaceutical manufacture
Organic peroxide manufacturing wastes
Ethylene bromide manufacturing wastes
Urethane manufacture wastes

180 kg/s (17,000 tons per day) (wet basis) for this application alone. There are currently numerous industrial installations in operation which are primarily utilized for chemical sludge and tar incineration as well as activated carbon regneration[12].

Operation Principle--

The multiple hearth furnace consists of a refractory-lined circular steel shell with refractory hearths located one above the other (Figure 5). Sludge and/or granulated solid combustible waste feeds through the furnace roof by a screw feeder or belt and flapgate. A rotating air-cooled central shaft with air-cooled rabble arms and teeth plows the waste material across the top hearth to drop holes. The waste falls to the next hearth and then the next until ash discharged at the bottom. The waste is agitated as it moves across the hearths to make sure maximum surface is exposed to hot gases. Waste grease and tars are generally fed into the furnace through side ports.

Liquid and gaseous combustible wastes may be injected into the unit through auxiliary burner nozzles. This utilization of liquid and gaseous waste represents an economic advantage since the secondary fuel (e.g., natural gas, fuel oil) requirements will be reduced thus lowering oprating costs.

The system has three operating zones: the top hearths where feed is dried to about 48 percent moisture; the incineration/deodorization zone, which has a temperature of 1030 to 2260 K (1400 to 1800 F); and the cooling zone, where the hot ash gives up heat to incoming combustion air. Exhaust gases exit at 530 to 860 K (500 to 1100 F).

Incineration ash is sterile and inert. Volume discharged from the bottom hearth is about 10 percent of the furnace feed, based on sludge cake with 75 percent moisture and 70 percent volatile content in the solids. The ash usually has less than 1 percent combustible matter, which is normally fixed carbon. Discharge can be moved hydraulically, mechanically, or pneumatically, and used as landfill or roadfill.

Current systems include gas cleaning devices on exhaust air. A number of multiple hearth incinerators are operating without difficulty in areas

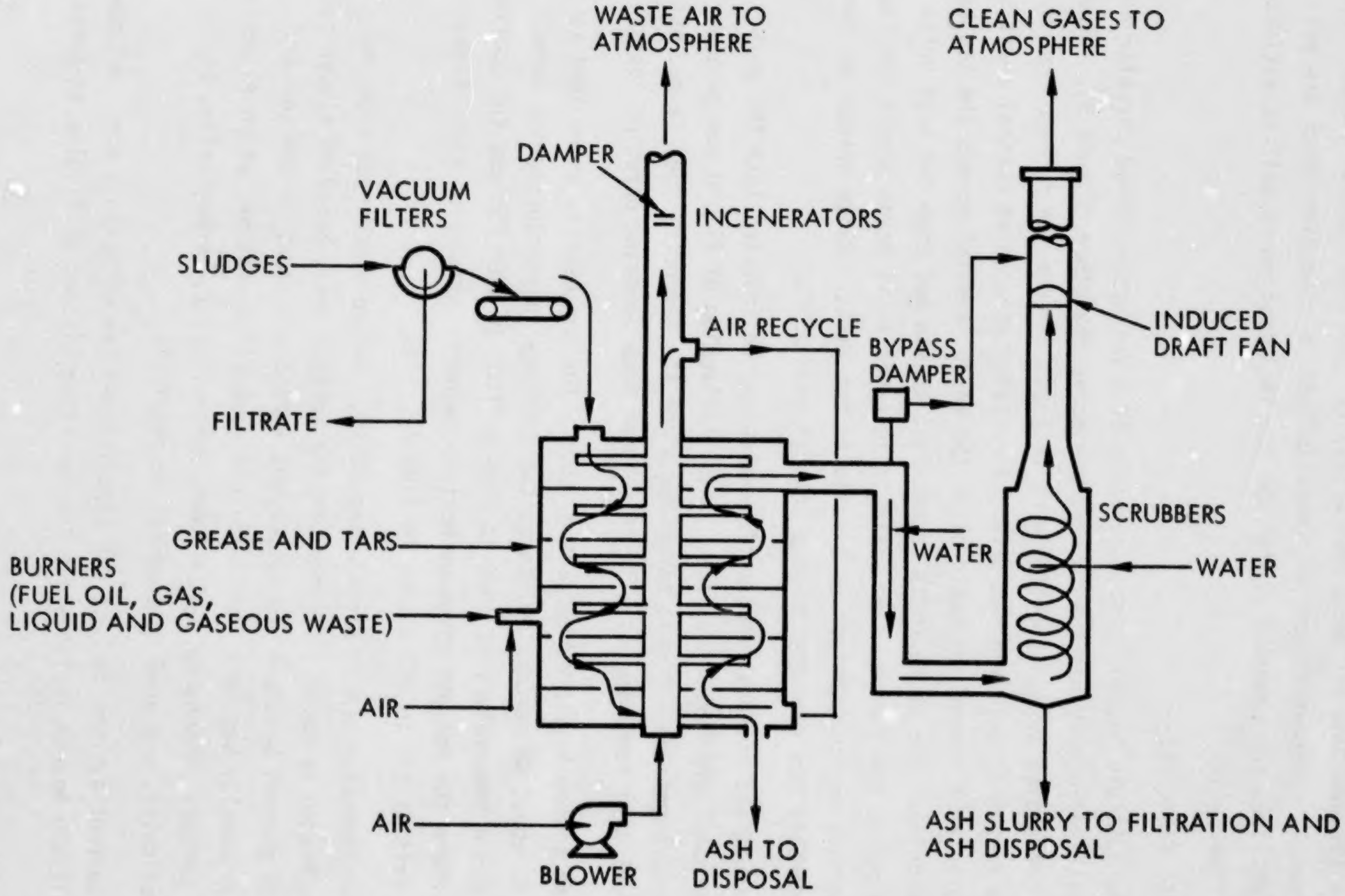
WASTE AIR TO ATMOSPHERE
CLEAN GASES TO ATMOSPHERE
DAMPER
VACUUM FILTERS
INCENERATORS
SLUDGES
INDUCED DRAFT FAN
AIR RECYCLE
BYPASS DAMPER
FILTRATE
SCRUBBERS
GREASE AND TARS
WATER
WATER
BURNERS (FUEL OIL, GAS, LIQUID AND GASEOUS WASTE)
AIR
AIR
BLOWER
ASH TO DISPOSAL
ASH SLURRY TO FILTRATION AND ASH DISPOSAL

Figure 5. Multiple hearth incineration system.

with strict air pollution codes. Although the exhaust does not violate opacity codes, existence of steam plumes has on occasion caused adverse public reaction.

Process Design--

Most multiple hearth incinerators are primarily designed for sludge disposal. The other forms of waste which are simultaneously fed to the system are usually considered a heat source to be utilized during sludge incineration. A heat balance across a multiple hearth furnace must consider the heat absorbed by: latent heat in free moisture and combustion moisture, sensible heat in combustion gases, excess air, ash, radiation and shaft cooling. These quantities are balanced against the heat evolved from the combustibles in sludge solids and the fuel. Below is a typical analysis of sewage sludge combustibles.

C	59.8 percent
H_2	8.5
O_2	27.5
N_2	4.2
	100.0 percent

Calorific value of this sludge is 23 MJ/kg (10,000 Btu/lb).

Sludge parameters that have the most influence over incineration are moisture content, percent volatiles and inerts, and calorific value. Moisture is the principal one over which the plant operator has some control. Minimum moisture is important because of its thermal load on the incinerator.

Volatiles and inerts, which affect the calorific value of the sludge, can be controlled to some extent by treatment processes such as degritting, mechanical dewatering and sludge digestion. Almost all combustibles are present as volatiles, much in the form of grease. Volatile percentage can vary a great deal, so equipment must be designed to handle a range of values.

The sizing of a multiple hearth incinerator is dependent upon waste combustion characteristics (Table 3) and water content. Incineration burning rates vary from 0.009 $\text{kg/m}^2\cdot\text{s}$ to 0.016 $\text{kg/m}^2\cdot\text{s}$ (7 to 12 $\text{lb/ft}^2\text{-hr}$) for sewage plant sludges with the value 0.01 $\text{kg/m}^2\cdot\text{s}$ (7.5 $\text{lb/ft}^2\text{-hr}$) generally

TABLE 3. TYPICAL COMBUSTION VALUES OF WASTE MATERIALS

Material	Combustible,%	Ash,%	MJ/kg (Btu/lb.)
Grease & scum	88.5	11.5	39.0 (16,750)
Fresh sewage solids	74.0	26.0	23.9 (10,285)
Fine screenings	86.4	13.6	20.9 (8,990)
Ground garbage	84.8	15.2	19.2 (8,245)
Rags	97.5	2.5	18.7 (8,050)
Digested sewage and garbage solids	49.6	50.4	18.7 (8,020)
Digested sludge	59.6	40.4	12.3 (5,290)
Grit	33.2	69.8	9.3 (4,000)

Note: Where organic polymers can be utilized to condition sludges, rather than ferric chlorides and lime, the heat value of the sludge cake can be increased from 3.5 to 9.3 MJ/kg (1,500 to 4,000 Btu/lb) of dry solids. The ash from the furnace will also be reduced by 5 to 10 percent.

accepted as typical. The area referred to in the burning rate is the total hearth area of the unit. Standard multiple hearth incineration sizes range from 7.9 m^2 (85 ft^2) of hearth to greater than 278 m^2 (3000 ft^2) of hearth (Table 4). The secondary fuel requirement is dependent upon the water content of the waste being incinerated. For instance, a waste sludge with a heating value of 23.2 MJ/kg (10,000 Btu/lb) of volatile solids which is composed of 60 percent volatile solids, will require about 3 m^3 of natural gas per thousand kg (100 ft^3/ton) of wet feed when the moisture content of the sludge is 75 percent. The same sludge will require about 37 m^3 of gas per thousand kg (1200 ft^3/ton) of wet sludge when the moisture content is 82.5 percent.

The multiple hearth incinerator is usually operated so that the top hearth temperature is in the 590 to 810 K (600 to 1000 F) range, the combustion hearths are in the 1030 to 1260 K (1400 to 1800 F) range, while the cooling hearths are maintained in the 480 to 590 K (400 to 600 F) range.

2.5.4 Rotary Kiln Incinerators

Rotary kiln incinerators are versatile units which can be used to dispose of solid, liquid and gaseous combustible wastes. They have been utilized in both industrial and municipal installations. In addition, applications of rotary kiln incineration to the disposal of obsolete chemical warfare agents and munitions have been reported[12].

Operation Principle--

The rotary kiln incinerator is a cylindrical shell lined with firebrick or other refractory and mounted with its axis at a slight slope from the horizontal. It is a highly efficient unit when applied to solids, liquids, sludges and tars because of its ability to attain excellent mixing of unburned waste and oxygen as it revolves. Its use as a concentrated waste gas combustor is considered a secondary application. This is due to the fact that although proper conditions are present for efficient gas combustion (i.e., long residence time at elevated temperatures) there is no need for the cylinder to be rotating. Therefore rotary kiln incinerators are used for gaseous waste combustion only in conjunction with solid or liquid waste incineration.

Rotary kiln incinerators used in municipal applications are generally desgined to handle large volumes of solid combustible waste (refuse) along

TABLE 4. STANDARD MULTIPLE HEARTH FURNACE SIZE

Outside diameter		4 Hearth	6 Hearth	8 Hearth	10 Hearth	12 Hearth
4.5 ft* (ID)	Hearth area,sq ft		85	112	140	
	Column height, ft-in.		4-0	4-0	4-0	
	Shell height, ft-in.		10-6	13-8	16-10	
	Overall height, ft-in.		15-7	18-9	21-11	
7.0 ft	Hearth area, sq ft		125	166	208	
	Column height, ft-in.		4-0	4-0	4-0	
	Shell height, ft-in.		11-10	15-5	19-0	
	Overall height, ft-in.		16-1	20-6	24-1	
8.5 ft	Hearth area, sq ft	130	193	256	319	
	Column height, ft-in.	5-0	5-0	5-0	5-0	
	Shell height, ft-in.	10-10	15-5	20-0	24-7	
	Overall height, ft-in.	16-7	21-2	25-9	30-4	
10.0 ft	Hearth area, sq ft	188	276	364	452	
	Column height, ft-in.	6-6	6-6	6-6	6-6	
	Shell height, ft-in.	10-8	15-1	19-5	23-10	
	Overall height, ft-in.	18-8	23-0	27-5	31-9	
13.5 ft	Hearth area, sq ft	390	575	760	944	1128
	Column height, ft-in.	6-6	6-6	6-6	6-6	6-6
	Shell height, ft-in.	11-8	16-7	21-5	26-4	31-2
	Overall height, ft-in.	20-8	25-6	30-5	35-3	40-2
16.0 ft	Hearth area, sq ft	573	845	1117	1305	1550
	Column height, ft-in.	7-0	7-0	7-0	7-0	7-0
	Shell height, ft-in.	13-2	18-7	24-1	29-6	35-0
	Overall height, ft-in.	22-11	28-4	33-10	39-3	44-9
18.0 ft	Hearth area, sq ft	727	1068	1410	1752	2090
	Column height, ft-in.	7-0	7-0	7-0	7-0	7-0
	Shell height, ft-in.	14-3	20-2	26-0	31-11	37-9
	Overall height, ft-in	24-3	30-1	36-0	41-10	47-9
19.5 ft	Hearth area, sq ft	863	1268	1660	2060	2464
	Column height, ft-in.	8-0	8-0	8-0	8-0	8-0
	Shell height, ft-in.	14-4	20-2	26-1	31-11	37-10
	Overall height, ft-in.	25-8	31-7	37-5	43-4	49-2
21.5 ft	Hearth area, sq ft	1077	1580	2084	2570	3046
	Column height, ft-in.	8-0	8-0	8-0	8-0	8-0
	Shell height, ft-in.	16-1	22-9	29-6	36-2	42-11
	Overall height, ft-in.	27-9	34-6	41-2	47-11	54-7

*English units are used in this table because the furnaces sizes in the United States are quoted in these units. See Unit Conversion Table.

with any entrained liquid. In this type of facility, the kiln actually serves as a secondary combustion unit since the waste material is ignited on traveling grates prior to entering the kiln (Figure 6). In this instance, the kiln serves mainly as an efficient mixer of the burning waste with combustion air.

Rotary kiln incinerators when applied to industrial applications are generally designed to accept both solid and liquid feed. A typical major industrial installation is operated by the Dow Chemical Company at Midland, Michigan (Figure 7). This particular unit consists of a 19 MW (65 million Btu/hr) kiln that is used for the incineration of solid chemical refuse, liquid residues, paper, wood and other solids of varying calorific content. A pack-feed mechanism is used to feed packs and drums of solid waste chemicals into the incinerator.

Liquid wastes transported to the incinerator are transferred to designated receiving tanks that contain compatible wastes. All drums of liquid wastes are also transferred to the receiving tank by the way of a drum-dumping dock. The waste is strained as it is pumped from the receiving tank into a burning tank, where it is blended for optimum burning characteristics. All liquid residues are burned in suspension by atomization with steam or air.

Drum quantities of solid tars are destroyed by feeding them into the rotary kiln incinerator via a hydraulically operated drum and pack-feeding mechanism. All refuse, except full drums and packs of material, is dumped into the refuse pit. An overhead crane is used to mix the refuse and raise it to the charging hopper of the rotary kiln (see Figure 7).

While the solid refuse is being fed, liquid tars are fired horizontally into the rotary kiln. As the refuse moves down the kiln, organic matter is destroyed, leaving an inorganic ash. This ash is made up primarily of slag, and other nonburnables such as drums and other metallic material. The ash discharges from the end of the kiln into a conveyor trough that contains water. After quenching, the material is conveyed into a dumping trailer, and then to a landfill.

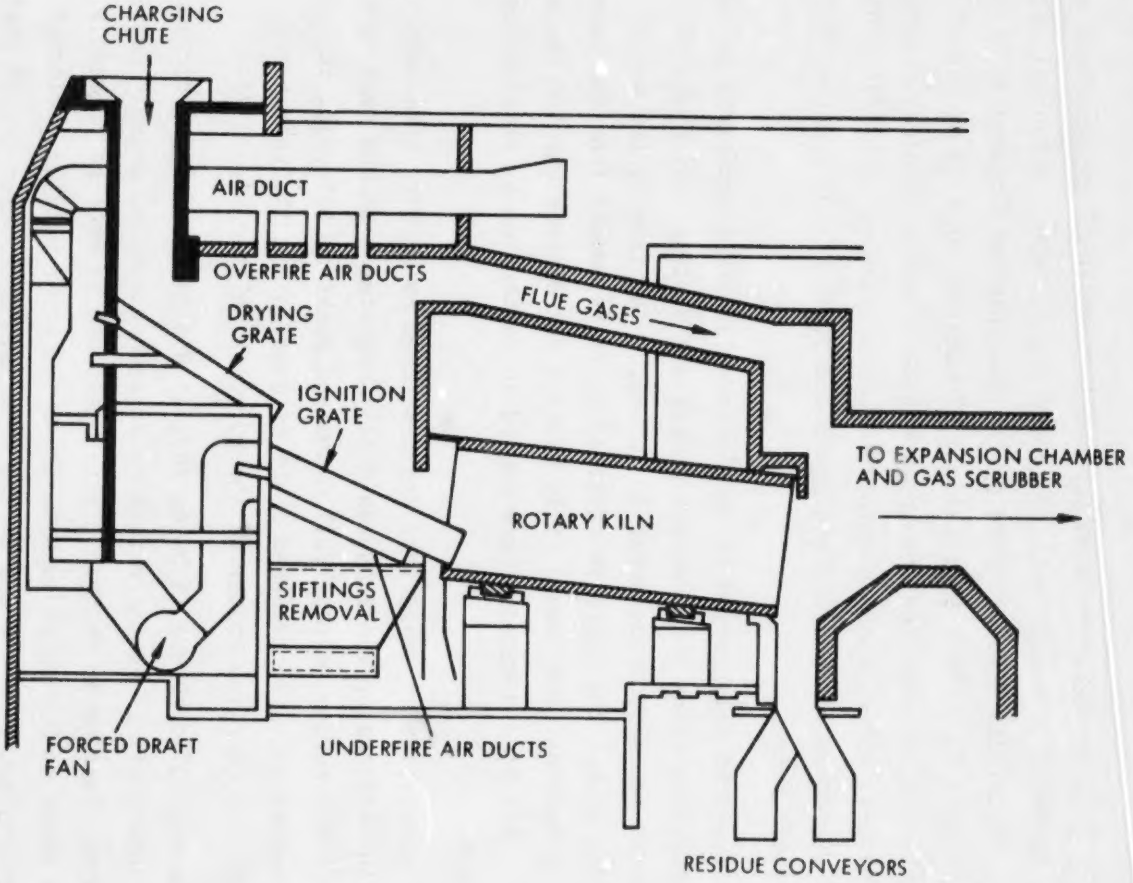
CHARGING CHUTE
AIR DUCT
OVERFIRE AIR DUCTS
DRYING GRATE
IGNITION GRATE
FLUE GASES
ROTARY KILN
TO EXPANSION CHAMBER AND GAS SCRUBBER
SIFTINGS REMOVAL
FORCED DRAFT FAN
UNDERFIRE AIR DUCTS
RESIDUE CONVEYORS

Figure 6. Municipal rotary kiln incineration facility.

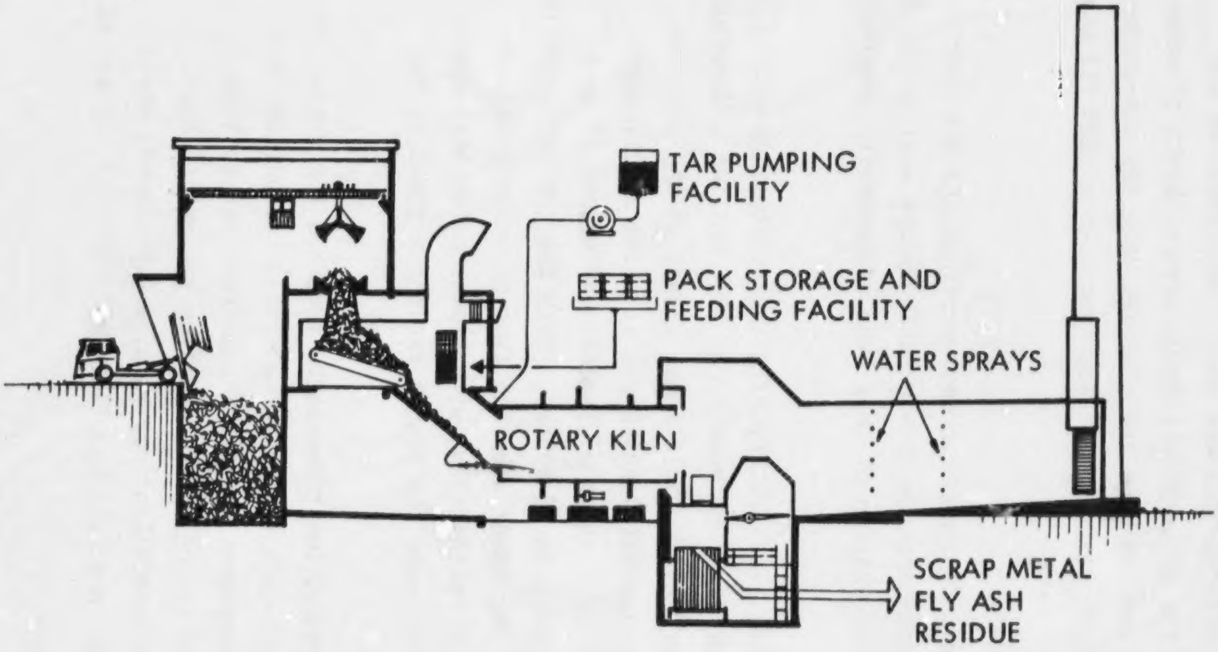
TAR PUMPING FACILITY
PACK STORAGE AND FEEDING FACILITY
WATER SPRAYS
ROTARY KILN
SCRAP METAL
FLY ASH
RESIDUE

Figure 7. Typical major industrial rotary kiln incineration facility.

After leaving the kiln, the products of combustion enter the secondary combustion chamber and impinge on refractory surfaces that cause a swirling action. No secondary fuel or afterburners are used. Downstream of the secondary combustion chamber, the gases pass through several banks of water sprays in which the flyash in knocked down and slurried into the ash-conveyor floor. Cooled gases pass under a stack damper and then a 61 m (200 ft) stack.

Process Design--

Specific data on rotary kiln incinerator design parameters are scarce. This is due to the fact that incineration is a relatively new application for rotary kilns. Additionally, information of this type is generally considered proprietary by manufacturers.

Information sources indicate that rotary kiln incinerators generally have a length to diameter ratio (L/D) between 2 and 10. Smaller L/D ratios result in less particulate carry over. Rotational speeds of the kiln are usually much slower than those for kilns which are utilized as calciners or dryers and are on the order of 5 to 25 millimeter per second (1 to 5 feet per minute) measured at the kiln periphery. Both the L/D ratio and the rotational speed are strongly dependent upon the type of waste being combusted. In general, larger L/D ratios along with slower rotational speeds are used when the waste material requires longer residence times in the kiln for complete combustion.

The residence time and combustion temperature required for proper incineration is totally dependent upon the waste materials combustion characteristics. Combustion temperatures usually range from 1140 to 1920 K (1600 to 3000 F). Required residence times vary from seconds to hours. For instance, a finely divided propellant may require 0.5 seconds while wooden boxes, municipal refuse, and railroad ties may require 5, 15 and 60 minutes respectively.

Process Applicability--

The rotary kiln incinerator is generally applicable to the ultimate disposal of any form of combustible waste material and represents proven technology. It can incinerate combustible solids (including explosives), liquids (including chemical warfare agents), gases, sludges and tars. Table 5 gives a partial list of wastes currently incinerated in rotary kiln.

TABLE 5. WASTES CURRENTLY INCINERATED IN ROTARY KILNS

Epichlorohydrin manufacturing wastes
Steam still bottoms from aniline and alkylated phenol production
Acryonitrile manufacturing wastes
Reactor tar bottoms from adrysonitrile manufacture
Phenolic tar from 2,4-D manufacture
Chlorotoluene production wastes
Phenylamine tar wastes
PCB wastes in capacitors
Evaporate residue from the cumere process for phenol manufacture
Nitrochlorobenzene tars
Catch basin grease, nitrile pitch from production of surface active agents
TDI manufacture reactor tar bottoms
Diphenylamine manufacture reactor for bottoms
Mercaptobenzothiazale tars

SECTION 3

CHARACTERIZATION OF INCINERATORS FOR THE SAFE DESTRUCTION OF HAZARDOUS WASTES

3.1 GENERALITIES

The safe destruction of hazardous wastes by incineration depends on the exposure of the hazardous components to oxygen at sufficiently high temperatures for a sufficient time to promote either combustion or decomposition These are also the conditions that lead to complete combustion of fuel. Thus, safe waste destruction, exactly like all combustion, depends on temperature, residence time and turbulence (or mixing of reactants). Temperature levels and residence time needed for the destruction of any given specie can be determined in the laboratory. The capability of any given incinerator to provide an adequately high temperature and residence time (including generous safety margins) can also be established, through measurements and calculations. When necessary, auxiliary fuel will be burned to insure desired temperature levels, and waste, fuel and air flow rates will be adjusted to meet the residence time requirements, on the average. Evaluation and control of mixing are more difficult, because the overdesign or "safety factor" approach is not readily applicable. More sophisticated approaches than overdesign are needed to ensure the desired destruction efficiency for a given waste or waste component in a given incinerator, and to permit scale-up of proven designs to a larger capacity system. Mathematical modeling of the heat and mass exhange mechanisms and of reactant flows has been attempted in some cases, with limited success. Collection of voluminous data and application of regression analysis and other statistical methods have also been proposed. The sheer size of a program necessary to obtain models adequately representing a system as complex as an incinerator burning non-gaseous material can be imagined by recalling the massive effort expended in modeling liquid propellant combustion in rocket motors - a much simpler system than a waste incinerator. On the other hand, a "data crunching" approach, when not supported by some understanding of the underlying laws of physics, demands an inordinately large amount of data in order to have a chance of succeeding.

So far the most promising avenue is a judicious mixture of simple mathematical models and data to "tune" these models. By gradually developing the analytical tools (in conjunction with experimental R&D) and acquiring a data base from measurements obtained on industrial systems one can expect to arrive at useful scale-up laws and reliable prediction of hazardous waste destruction efficiencies.

The development of analytical tools mainly consists of the study and description of physical phenomena in terms of appropriate non-dimensional parameters, involving the expression of basic laws or the establishment of correlations. For instance, the combustion of liquid fuels and wastes depends on liquid atomization and jet mixing. Correlations in this field are available and can be used to evaluate liquid destruction inefficiency and to estimate liquid jet penetration for a scaled-up system. On the other hand, correlations permitting the evaluation of the degree of mixing in a fluidized bed are not as yet established. In the following discussion of the four incinerator types, the present state of knowledge is summarized and the possibilities of using what knowledge is available to evaluate the incinerator effectiveness and the approach to scale-up of existing designs are indicated.

3.1.1 Combustion and Waste Destruction Efficiencies

The goal of hazardous waste incineration is the complete destruction of hazardous species, which is related to, but not identical with, the complete combustion of the fuel and of the combustible waste components. Sufficient information on the destruction efficiency of hazardous species in an incinerator is most often not available. Therefore, in the absence of directly applicable data, the overall combustion efficiency and other, experimentally accessible, destruction efficiencies may be useful for the purpose of predictive modeling or other approaches to prediction of hazardous species destruction. Since the ability to define a destruction efficiency in terms of measurable quantities is crucial, and since hazardous waste components are many and varied, the definition of destruction efficiencies will also vary to some extent.

A useful example of a generally applicable set of definitions is shown in Tables 6 and 7. These are the definitions adopted by TRW for the incineration at sea of the Herbicide Orange[13]. The overall combustion efficiency is defined in terms of CO_2 and CO; both are measurable quantities. Hydrogen and sulfur analysis were not included, because neither of these combustibles were important in the case of Herbicide Orange (HO) incineration. Note that the destruction efficiencies of HO as well as that of the two toxic contaminants chlorinated hydrocarbon (CHC) and of 2,3,7,8 - tetra chlorodibenzo-p-dioxin (TCDD), were found to be so high that their emissions were only marginally measurable, as shown in Table 7.

In the case of solid wastes incineration, solids carry over in the stream, as well as solids in the liquid effluents and in the solids residue, must be evaluated and measured. In most cases, the destruction efficiency can be defined as [(material fed - (material emitted)]/[material fed]. The exceptions are cases were hazardous species are created in the course of incineration. Then alternate, ad hoc definitions must be developed.

A more convenient form of the above expressions would be a destruction inefficiency, i.e., the ratio of quantity of material not destroyed to the material fed. This would replace the 99.999 ... percent by 100 - 99.999 = O 10^{-n} percent, or ppm, ppb etc., which speak more readily to the imagination.

3.1.2 Continuous, Batch and Periodic Operation

Destruction efficiencies, as defined above, could be applied to operations which include transient and cyclic operations, provided measurements of materials fed and emitted are taken over an appropriate period of time. Note that batch introduction of waste into an incinerator, such as dumping big drums into a rotary kiln, may result in a temporary overloading of the incinerator and of the effluent scrubbing systems. The resulting destruction efficiency will be much lower than if the material were introduced at a steady rate. Reduction of pollution could be achieved by an operating

TABLE 6. DEFINITION OF INCINERATION EFFICIENCY TERMS

Efficiency term	Method of calculation
Overall combustion efficiency	$DE_{CE} = 100 \times \frac{[\ \%\ CO_2\ ] - [\ \%\ CO\ ]}{[\ \%\ CO_2\ ]}$
Total hydrocarbon (THC) destruction efficiency	$DE_{THC} = 100 \times \frac{[\ \text{THC fed}\ ] - [\ \text{THC found}\ ]}{[\ \text{THC fed}\ ]}$
Herbicide Orange (HO) destruction efficiency	$DE_{HO} = 100 \times \frac{[\ \text{HO fed}\ ] - [\ \text{HO found}\ ]}{[\ \text{HO fed}\ ]}$
TCDD destruction efficiency	$DE_{TCDD} = 100 \times \frac{[\ \text{TCDD fed}\ ] - [\ \text{TCDD found}\ ]}{[\ \text{TCDD fed}\ ]}$
Chlorinated hydrocarbon (CHC) destruction efficiency	$DE_{CHC} = 100 \times \frac{[\ \text{CHC fed}\ ] - [\ \text{CHC found}\ ]}{[\ \text{CHC fed}\ ]}$

TABLE 7. SUMMARY OF CALCULATED INCINERATION EFFICIENCIES

	First burn	Second burn	Third burn	Combined 3 burns
DE_{CE}	99.992	99.989	99.983	99.990
DE_{THC}	99.982	99.992	-(a)	99.985
DE_{HO}	>99.999	>99.999	>99.999	>99.999
DE_{TCDD}	>99.99	>99.88	>99.96	>99.93
DE_{CHC}	>99.999	>99.999	>99.999	>99.999

(a) HC Analyzer was inoperative during third burn procedure modification and would not require modification of the incinerator proper. In the following work only steady state operation is considered.

3.1.3 Design of Large Scale Incineration Units

The manufacturers of incinerators and furnaces have generally been very conservative in their approach to scaling up their units; this is not surprising since designs were largely based on past experience with little analytical background to give confidence in an economically risky endeavor. Even today there are no scaling laws applicable to any one of the major incinerator types, not even for the liquid injection furnace, the device for which much prior research is available. It is somewhat misleading to talk about overall scaling laws, since larger units will not be geometrically scaled small units, but may utilize multiple subsystems. For instance, a large furnace will have multiple burners of the same size as used in a smaller unit, and a large fluidized bed will need several waste feed points rather than larger feed ports. The scaling laws, still to be developed, will most likely address the reproduction in a larger unit of favorable operating conditions developed in smaller ones. If good analytical tools are developed permitting this to be accomplished, then very large units could be designed without going through the design and operation of intermediate size devices. The economic advantages of skipping to large systems, such as are needed to address the ever growing quantity of hazardous wastes, are clear.

3.2 LIQUID INJECTION WASTE INCINERATION

Liquid injection waste incinerators are furnaces fired with liquid fuels which can be the waste itself or an auxiliary fuel, or a combination of both, depending on the heat content and combustion characteristics of the waste. A great deal of work, experimental and analytical, has been done to enhance the art of furnace design. This work should be very valuable in the prediction of pollutant emissions levels from hazardous waste incineration.

The overall temperature level and residence time in the incinerator are reasonably well known, both from measurements and analysis, and can be so chosen as to result in very high hazardous waste destruction levels. The effects of turbulence are more elusive. Analytical examination of the overall phenomena in furnaces relies on modeling of the overall heat and gas flows, and yields accurate prediction of gas temperature histories, but generally does not permit evaluation of the pollution levels of stack emissions.

There are two sources of incomplete destruction of hazardous components:

- Carry over of liquid droplets
- Carry over of unreacted vapor

The survival of liquid droplets depends on the atomization and penetration of the liquid jet, as well as the droplet or spray combustion, while carry over of unreacted vapors depends on recirculation and turbulence phenomena.

In the following subsections, the use of furnace models to establish the temperature and residence time is described, followed by discussions of the work on fuel atomization, droplet and spray combustion and turbulence. Approximate prediction of probable emission levels of hazardous species can be attempted for a given furnace and a given waste material by combining all of the above elements.

3.2.1 Analytical Models of Liquid Injection Incinerators

Destruction of hazardous waste components in any given incinerator depends on the same "three T's" as combustion in general, i.e., on Temperature, residence Time and Turbulence. If a detailed characterization of the hydrodynamic and chemical phenomena in the incinerator, i.e., if a complete mathematical model for the combustion in the incinerator were available, then the degree of waste destruction could be predicted. Mathematical modeling of liquid injection furnaces or combustion chambers has not reached such a state of development. Traditionally these devices are designed and operated on the basis of past experience guided by engineering insight. Some of the larger manufacturers of boilers and furnaces have initiated mathematical modeling efforts and it would be interesting to determine to what extent this is also true of incinerator manufacturers.

Most work on combustion chamber modeling applicable to liquid injection incinerators pertains to boilers and gas turbine combustors. The simplified models described in the literature are essentially one-dimensional and utilize either a system comprised of a stirred reactor (PSR) followed by a plug flow reactor (PFR) or the zone method[14]. The PSR-PFR system has been particularly useful in predicting such combustor performance characteristics as flame temperature, combustion intensity, extinction limits and combustion efficiency in radiant boilers.

The PSR-PFR Model--

In this model, the combustion chamber is divided into two sections. The first section, the PSR, includes the fuel injector and air inlet region, and the volume occupied by the flame. In this portion, all reactants are assumed to be perfectly mixed and are at a uniform temperature. The gas stream leaves the PSR with that same composition and temperature. The incoming stream to the PSR is composed of air and fuel, as shown in Figure 8. The reaction between fuel and air releases a major part of the heating value of the fuel in the PSR sections; combustion is complete in the second section, the PFR, in which a uniform flow of gases is postulated. The gas velocity and temperature vary from entrance to exit as part of the heating value is released and heat is lost to the walls.

Heat transfer to the combustion chamber walls is predominantly by radiation in the PSR, and by radiation and convection in the PFR sections. A simplication that may be acceptable in refractory lined furnaces is to neglect heat transfer to the walls. The function of the PSR section is to insure ignition and stable flame holding, that of the PFR to allow complete fuel combustion. The division into the two sections is made on the basis of visible flame boundary observation or from past experience.

Liquid fuel atomization characteristics and the velocity and direction of the incoming air influence the extent of the zone that should be included in PSR volume; penetration of the largest droplets, as well as the velocity of the atomizing fluid (air or steam) determine the length of liquid spray and therefore influence the flame length, though the PSR assumption is that all the incoming material is instantaneously and uniformly distributed and hence does not permit to include explicitly any such influence. The plug flow reactor section must allow for enough residence time to complete the combustion.

The Zone Method--

The zone method provides a more detailed model of combustion. However, the initial point is again an assumed knowledge of the fluid flow patterns, of the chemical reactions and of the radiation characteristics of the gases and solid particles (if any). The above assumptions are derived from experience acquired in similar systems and from simple empirical theories on the mixing behavior of confined jets.

The model is established as follows: The furnace volume and its walls are divided into a number of gas and surface "zones"; in each zone the temperature and properties are assumed to be uniform and the gas flows in and out of each zone known. A schematic of the models shown in Figure 9. Energy balances are then drawn for each zone, taking into account all forms of energy transport and including heat released or absorbed by chemical reactions. The solution of the many simultaneous energy conservation equations yields the temperature distribution in the furnace. Since the flow patterns, including perfect mixing inside

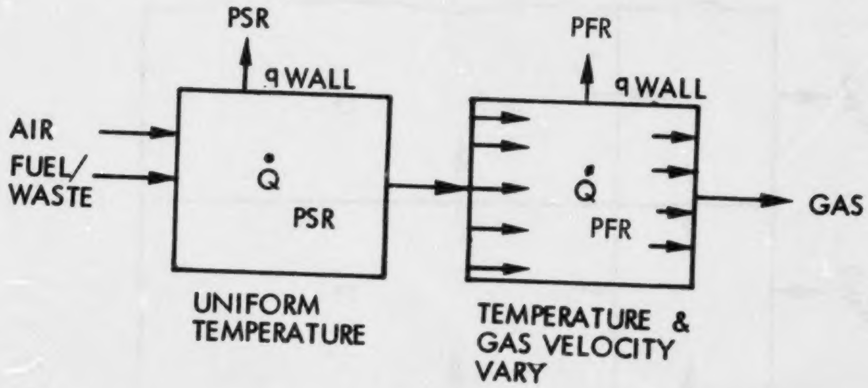

Figure 8. Perfectly stirred reactor/plug flow reactor (PSR/PFR) model of a liquid injection incinerator.

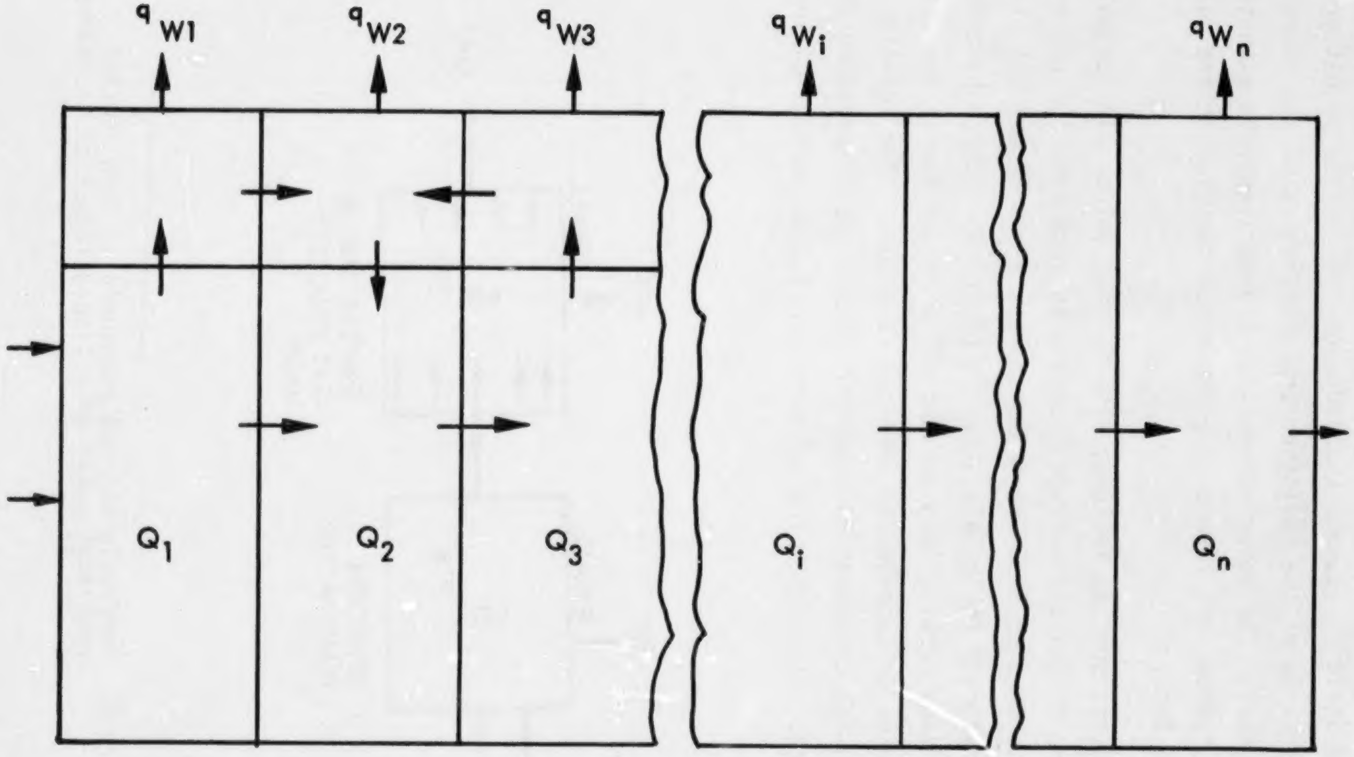
q_{W1}
q_{W2}
q_{W3}
q_{W_i}
q_{W_n}
Q_1
Q_2
Q_3
Q_i
Q_n

Figure 9. Zone model of a liquid injection incinerator.

each zone, were assumed to be known a priori, all three T's are now known, hence the combustion efficiency and the waste destruction efficiency can be derived. The difficulties stem from the underlying assumptions more than from the computational difficulties encountered in solving a large number of strongly nonlinear simultaneous equations (e.g., the radiation equation involving the fourth power of the temperature and Arrhenius type reaction rate equations involving exponential functions of the reciprocal of the temperature), though a great deal of effort is now devoted to developing time saving computational methods. The initial assumption that recirculation patterns in the furnace are known is weak, and so is our knowledge of the radiative properties of gases during combustion. Analysis of radiation from nonluminous flames, i.e., from gas containing CO_2, CO, H_2O, H_2 etc., is soundly based. However, soot is formed during combustion of most liquid and solid fuels and the presence of soot drastically increases the gas emissivity[15]. Soot concentrations are known to depend on temperature, the presence of water vapor and other hydrogen compounds and on the molecular weight of fuel constituents, but correlation between gas emissivity and the above parameters are not as yet available. Therefore the development of a good, predictive zone model for any furnace depends to a large extent on the amount of data (gas temperatures, emissivities, recirculation patterns, turbulent mixing etc.) available from similar devices and on the skill of the analyst in using that data to "tune" the model.

Data Utilization in Modeling--

There are various ways of using experimental results to tune a mathematical model, but the underlying logic is essentially the same for most. It consists of writing some of the equations to be solved in a form that reflects the governing mechanisms and includes terms (coefficient, powers etc.) which will be adjusted to experimental results.

For instance, in a PSR-PSF model, the volume occupied by the flame, the flame emissivity and the portion of the total heating value of the fuel released in the flame zone (the PFR) are not known. However, the influence of atomization on the wall heat flux may be available from measurements effected with several injector orifice sizes. It will be shown in a subsequent portion of this report that the droplet diameters are approximately proportional to the square root of the injector diameter and that the length of the flame depends on the droplet diameter. By judicious use of appropriate adjustable coefficients, power laws etc., and of regression analysis of experimental data, the model can be adjusted to correctly calculate one or more quantities that can be measured. In our example, the split between PSR and PSF can be adjusted to yield correct wall heat fluxes. The validity of the model must then be checked in comparing computations to data not previously used to adjust the model. The validity of the model and its range of applicability will depend on the amount and quality of the data available for tuning and validation. Under the most favorable conditions, the data will include a well defined independent parameter whose effect on one of the mechanisms mathematically expressed in the model can be tracked. The cleanest approach to tuning obtains when each data parameter influences one of the tuning factors. Such an ideal condition rarely exists, but can be approximated by examining and adapting the analytical formulation of the model in the light of available (or obtainable) data.

The model can be developed with data obtained with nonhazardous fuels reasonably similar to the hazardous fuel and be used to predict hazardous materials destruction efficiency, provided, of course, that the fuel properties are adequately represented in the model formulation (e.g., heating values, viscosity, etc.). The temperature distribution and residence time computed by the model are in many cases sufficient to estimate the completeness of the decomposition of the waste component of interest (assuming of course that the decomposition rate as a function of temperature and time is known). Difficulties could be encountered if a waste decomposition rate varies very steeply in the range of temperatures encountered in the incinerator. For instance, there are difficulties in the prediction of nitrogen oxide production because the reaction rate is extremely sensitive to temperature. However, Bueters et al[16] succeeded in developing a zone model for a tangentially fired utility boiler which is accurate enough to predict nitrogen oxide formation[17]. It is probable that these authors had access to a great deal of data.

Effects of turbulence (or unmixedness) are not included in the models discussed here. In turbulent flow, adjoining eddies found inside a "zone" may not have the same composition (contary to the assumption of uniformity inside each zone). The probability of incomplete decomposition of waste vapor due to turbulence will have to be evaluated separately as long as the simplified PSR/PSF and zone models are used.

3.2.2 Liquid Atomization and Jet Penetration

Liquid jet atomization has been studied extensively and droplet size and penetration have been usually correlated in terms of the Weber Number ($We = \sigma/D_o/\rho_g V_g^2$), the droplet Reynolds Number ($Re = \rho_L V_g D_o/\mu_L$) and of the ratio of liquid and gas velocities[18,19]. Ingebo has developed correlations for the volume-mean droplet diameter, D_{30}, and for the maximum droplet diameter, D_{max}*, for the case of a simple, round injector orifice of diameter D_o. He has also verified experimentally a drop size distribution equation proposed by Nukiyama-Tanasawa (in a somewhat modified form).

Jet penetration into an air stream was also shown by Ingebo[20] to depend on the Weber and Reynolds Numbers and on the liquid to gas velocity ratio. The maximum penetration distance x_{max} is related to the maximum drop diameter D_{max}

$$x_{max}/D_{max} = 0.08\ Re\ We^{-0.41}(V_g/V_L)^{0.29} \qquad (1)$$

A priori calculation of droplet size and distribution for injectors other than simple round orifices, and for injectors with compressed air or steam addition, is not possible. Data is needed to develop the correlations for each given injector configuration. However, it is clear that the correlations will be reducible to the form

$$D/D_o = f(We,\ Re,\ V_l/V_g)$$

and that jet penetration correlations will be amenable to similar expressions.

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*These exists a D_{max}, since larger drops shatter, as discussed below. $D_{max} = 22.3\ D_o\ (We/Re)^{0.29}$

More recently M. C. Simmons[21] has established non-dimensional correlations for the drop sizes/volume fraction distribution and the drop size/number distribution for drop diameters normalized to a Mean Median Diameter or to a Sauter Mean Diameter. The correlations were developed for aircraft and industrial gas turbine nozzles, including pressure atomizers, air assisted and air-blast nozzles. (Industrial, steam atomizing nozzles may produce a different droplet size distribution.) The correlation plot is linear when a square root scale is used for the normalized drop diameter, and a normal probability scale for the cumulative volume less than the stated value of drop diameter. This fact allows computation using statistical tables of the relationship of $\sqrt{D/D_M}$ and the volume fraction. Similarly, Simmons has shown that the cumulative number of drops is a simple exponential function of the normalized drop diameter. He has also found evidence that for each fuel nozzle and operating condition there is a maximum drop size, above which the probability of survival is "vanishingly small", and that

$$D_{max} = 3\ D_{MMD} \quad \text{or} \quad = 3.6\ D_{SMD} \qquad (2)$$

for any given spray. Note that Ingebo also had found that such a maximum droplet diameter existed. More generally it has been found[22] that secondary break-up of droplets occurs at high relative velocities, the criterion for break-up being a critical Weber number of the order of 6 to 30 (depending on the Reynolds number). This finding is very important, since the residence time needed to evaporate a spray is a strong function of droplet diameter. The evaporation of the largest droplets influences the degree of completeness of combustion (or of any other reaction) of the injected liquid components.

Atomization of liquids by rotating cups has been examined by Hinze and Milborn[23], and found to depend on a Weber and a Reynolds number; though the authors chose somewhat different groups of properties to develop their correlations, their groups can be rearranged into Weber and Reynolds numbers.

The importance of the existence of the various correlations lies in showing how we can manipulate, for any given injector, the operating conditions so as to obtain the same atomization characteristics with several fuels; for instance, by heating a viscous fuel, altering the atomizing gas velocities or by using fuel mixtures, so as to maintain invariant the Weber and Reynolds Numbers. Thus, invariant liquid spray characteristics can be insured for fuels with different physical properties.

Modeling and scaling of the atomization is relatively straightforward, since cold flow experiments suffice to develop suitable correlations, or to verify the applicability of the existing ones, for the candidate injectors. These correlations then can be used in designing the incinerator. Jet penetration can also be experimentally investigated in cold flow. However, the influence of the internal gas flows, which depend on the furnace configuration and on the combustion-induced gas flows, is not fully represented by cold flow.

3.2.3 Droplet and Spray Combustion

The combustion of a spray of liquid fuel involves the combustion of fuel vapors and of the discrete droplets that make up the spray. The classical shrinking-sphere model of diffusion-controlled combustion in an oxidizing atomosphere is not sufficient to describe spray combustion; nevertheless, that model is fundamental to understanding spray combustion phenomena.

Droplet Combustion--

The simplest model of droplet combustion is the diffusion-controlled model of an isolated spherical droplet, when gas velocities are relatively low. This model is applicable to dilute sprays only. In dense sprays, complete evaporation of the droplets may precede burning, which then is controlled by the diffusion of the vapor into the air or by gas-gas mixing.

For dilute sprays, i.e., isolated droplets in quiescent air, a droplet evaporates and the fuel vapor and the air burn in a diffusion flame which surrounds the droplet. The mass burn rate $\dot{m}_L$ is related to the decrease in droplet diameter D such that[24]

$$\dot{m}_L = - \frac{d}{dt} \left(\pi \frac{D^3}{6} \rho_L \right) \qquad (3)$$

which can be rewritten as

$$\frac{d}{dt}(D^2) = -\frac{4\,\dot{m}_L}{\pi\rho_L D} \tag{4}$$

It has been shown experimentally that $\dot{m}_L$ is proportional to D, so that the above equation can be integrated to yield

$$D^2 = D_o{}^2 - Kt \tag{5}$$

In the above equation, the constant K must be obtained from experiment or by solving conservation equations for global mass, species mass, energy, and momentum.

Solution of the conservation equations is possible provided some major assumptions are made. These assumptions include:

- Infinitely rapid chemical reaction rate
- Simplified chemical reactions, such as,
  Fuel + O_2 → products, or
  Fuel + Oxygen → CO followed by CO + Oxygen → CO_2

The solutions depend on whether fixed or variable transport properties are used. A widely used model, assuming fixed properties and a Lewis Number of one,* results in a burning rate coefficient K

$$K = \frac{8\,\bar{\lambda}}{C_p\rho_L}\ \ln(1+B) \tag{6}$$

where the transfer number B is

$$B = \frac{1}{L}\left[C_p(T_\infty - T) + Q\phi\right] \tag{7}$$

and

$\bar{\lambda}$ = thermal conductivity of the gases
Q = fuel heating value
L = latent heat of evaporation
C_p = specific heat of gases
ϕ = equivalence ratio (air/fuel)/$(\text{air/fuel})_{\text{stoichiometric}}$

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*The Lewis Number is the ratio of thermal diffusion to gas diffusion coefficients.

The results markedly depend on the values assigned to the thermal conductivity $\bar{\lambda}$ and the specific heat C_p of the gases; these depend on gas temperature and composition, neither of which is known a priori. Usually $\bar{\lambda}$ and C_p are computed on the basis of air or nitrogen properties at the log mean temperature between the liquid and the flame temperature, though somewhat more sophisticated approaches have been proposed.

Incinerator fuels are mostly mixtures of hydrocarbons and other more or less volatile compounds, rather than a single component liquid. An expression for the burning rate coefficient of binary mixtures was derived by Wood, et al[25] and numerical calculations have been carried out for multicomponent heavy fuel oils[26]. The method proposed in the latter work could be used to compute the evaporation and combustion of a given compound (hazardous waste) contained in a liquid fuel. The compound could be liquid or a suspended solid, or a solid formed by fuel cracking, such as occur in heavy fuel oils. However the computation is cumbersome and a large computer is needed.

Equation (5) is valid for a droplet burning in quiescent air, whereas in most furnaces air velocities must be high enough to promote mixing. A correction of the burning rate to take into account forced convection has been proposed[27]

$$K_{\text{forced conv.}} = K_o \left[1+0.278\, Re_L^{1/2}\, Pr^{1/3}(1+1.237/Re_L Pr^{4/3})^{-1/2}\right] \quad (8)$$

This equation is possibly valid for $10<Re_L<800$ but has not been experimentally verified outside of the range $1.3<Re_L<2.2$.

Calculations of spray penetration into the combustion chamber are based on drag coefficients of evaporating droplets. Experimental work on evaporating and burning droplets have shown that the Reynolds Number is the dominating parameter in all flow regimes of interest. Dickerson and Sherman[28] have summarized all the data available in 1965 in terms of the droplet drag coefficient C_D:

$$C_D = 27\, Re^{-0.84} \qquad 0<Re\leq 80$$
$$C_D = 0.271\, Re^{0.271} \qquad 80<Re\leq 10^4$$
$$C_D = 2.0 \qquad Re>10^4$$

None of the proposed predictive methods can take into account transient burning effects or change in combustion mode, such as the transition, above a critical gas velocity, from a diffusion flame all around the droplet to a wake flame (i.e., no burning on the droplet surface and combustion in the wake behind the droplet). Still more important is the fact that the single droplet combustion model does not really represent spray combustion.

Spray Combustion--

It has been shown that droplets exist in a relatively small volume, close to the injector nozzle and that most droplets do not burn individually, but that the fuel vapor from the droplets burns in a jet, essentially as a gas diffusion flame. This was proven in experiments conducted with a light distillate oil[29] and with heavy fuel oil[30]. The "mixed is burned" principle applies well to a diffusion flame, i.e., the turbulent mixing of fuel vapor and air is the combustion rate controlling mechanism. Therefore, one would consider characterizing the droplet shrinking shown in equation (5), by heating and evaporation only and omit the fuel heat release time term $Q \times \Phi$ in equation (7) when modeling the incineration mechanisms as a spray, i.e., a gas-diffusion flame.

3.2.4 Turbulence and the Unmixedness Factor

Hawthorne, et al[31] have shown that in turbulence controlled combustion of gas sampling and concentration measurements yield data that permits calculation of an unmixedness factor $\sqrt{\overline{C'^2}}$, which in turn can be used to used to predict emissions of unburned or incompletely burned fuel components.

Figure 10 from Reference 31 shows the correlation between the unmixedness factor and the ratio of oxygen measured in a gas sample to the stoichiometric oxygen required to complete the combustion of fuel as measured in the sample (CO, H_2 or UHC).

Thus the unmixedness factor can be obtained at a point at which the gas is sampled. Often it is important to calculate the unmixedness factor at a point upstream of the point of sampling, which is usually far downstream of the flame region. For instance, if it is known that the destruction of a hazardous waste component cannot take place below a certain temperature, then

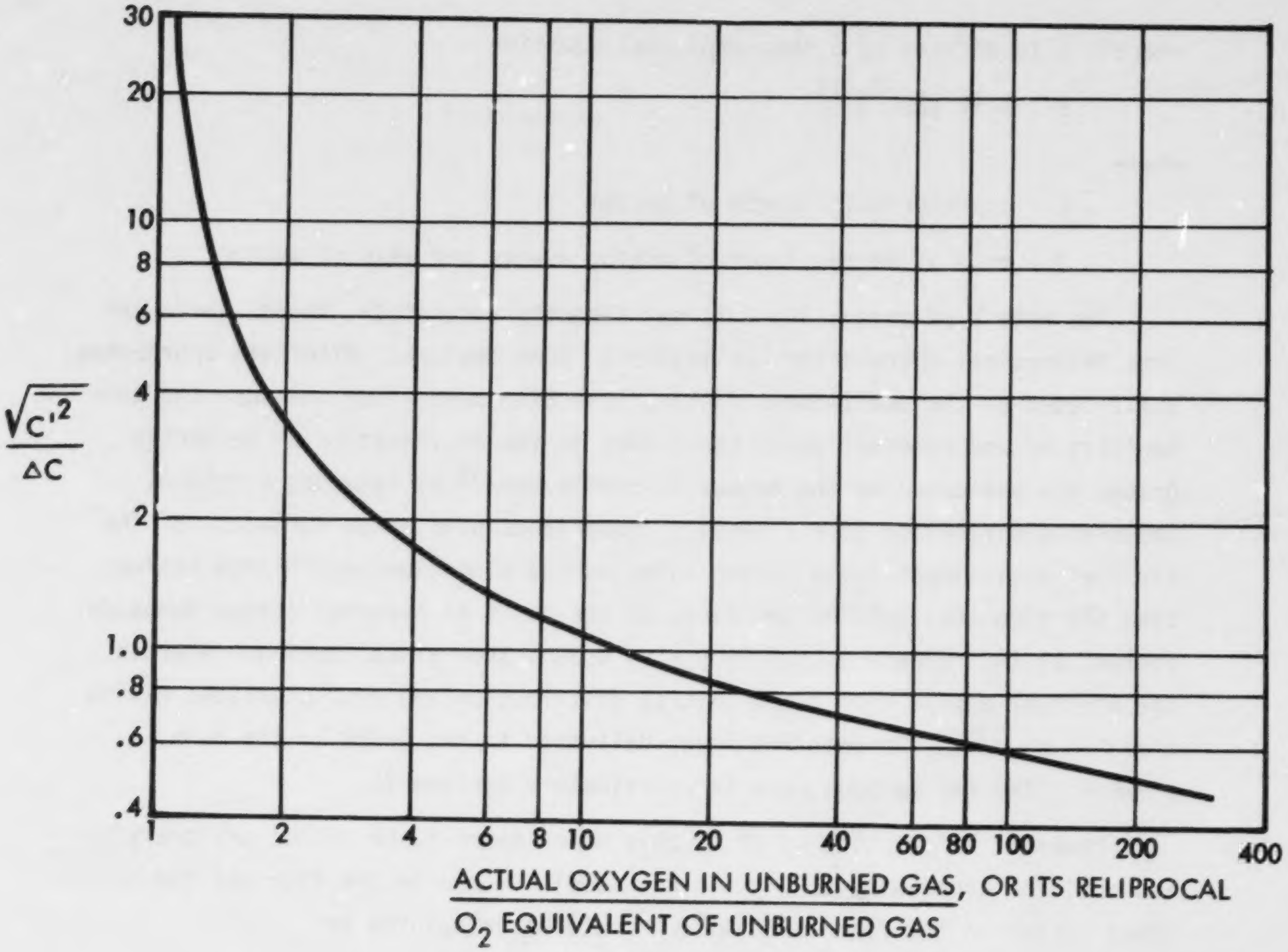


Figure 10. The unmixedness factor in turbulent flames.

the contribution to emissions of that component due to unmixedness will depend on the unmixedness factor in the region of the incinerator where the temperature drops to that level.

Unmixedness at points upstream of the sampling point can be inferred, if it is assumed (Reference 32) that unmixedness decay follows the same laws as turbulence decay - i.e.,

$$\frac{\sqrt{\overline{C'^2}}}{\sqrt{\overline{C'^2_0}}} = \exp(-\beta t)$$

wherein β is defined by a semi-empirical equation

$$\beta \equiv 0.19\ (\Sigma/L^2)^{1/3}$$

where

L = characeristic length of system

Σ = rate of energy input of mixing energy per mass of system

The rate Σ of energy input is not directly accessible, though there are some theoretical correlation applicable to some devices. Alternate approaches, still based on the unmixedness factor, have been used. For instance the probability of undecomposed vapor carry over in the incineration of Herbicide Orange was evaluated by the Arthur D. Little team[33] by assuming a typical Gaussian distribution (i.e., based on experience with other furnaces) of the air/fuel equivalence ratio at the inlet to the plug flow section and estimating the time constant for the decay on the basis of measured carbon monoxide content at the furnace exit. They also used a theoretical approach wherein the air/fuel equivalence ratio initial distribution and characteristic mixing time are based on the specific power delivered to the gases in the main chamber. The two methods were in satisfactory agreement.

However, calculation of βt by this means seems to be rather arbitrary and could be avoided by taking two gas samples - one in the flue gas the other closer to the flame zone; then β could be calculated as

$$\frac{\left(\sqrt{\overline{c'^2}}\right)_{t_1}}{\left(\sqrt{\overline{c'^2}}\right)_{t_2}} = \exp\left[-\beta(t_1-t_2)\right]$$

since (t_1-t_2) is known from the gas velocities and the distance between the two sampling locations.

3.2.5 Estimation of Hazardous Waste Destruction Inefficiencies

The three sources of liquid waste destruction inefficiencies are:

- carry over of unevaporated liquid droplets
- carry over of unreacted vapor due to inadequate temperature history
- carry over of unreacted vapor due to unmixedness

The following steps would lead to an estimation of an upper bound of destruction inefficiencies:

- Obtain the temperature and residence time required to achieve complete decomposition of the hazardous species.
- Characterize the liquid atomization and jet penetration of and fuel. Needed are the physical properties of the fuel/waste and cold flow experiments.
- Develop a PSF-PFR model of the incinerator. If measurements of flame temperature and wall heat flux are not available, engineering estimates based on fuel spray characteristics (cold flow tests) are possible. The model will yield the average temperature.

From the above, the probability of a drop surviving passage through the entire furnace and the probability of some (low) part of the vapor not reacting completely can be established.

- Obtain data on the carbon monoxide and oxygen content in the stack when burning a nonhazardous fuel with equivalent properties.

From these data, the portion of unreacted vapor due to unmixedness (adjoining eddies of fuel vapor and oxidizer) and to bypass of the main reaction zones (boundary layer flows and recirculation) can be estimated,

3.2.6 Summary

Despite the scope of the efforts expended to date in investigating the combustion of atomized liquid fuels in furnaces there is no generally applicable method to predict the composition of the flue gases with the precision needed to insure safe incineration of hazardous waste components. An approach to the estimation of an upper bound of hazardous component destruction inefficiencies has been proposed here. The success of the estimation depends to a large degree on the availability of experimental data because the theoretical base and analytical tools alone are insufficient.

3.3 FLUIDIZED BED INCINERATORS

Fluidized bed incinerators are reactors in which a bed of inert particulates (sand) is supported by a distribution plate through which air is flowing. Waste and auxiliary fuel are injected into the bed above the distribution plate. Fluidization occurs when the frictional forces between gas and a particle equal the weight of the particle. At this flow rate the bed is considered incipiently fluidized and the voidage of the bed is equal to the voidage of the most loosely packed fixed bed. An increase in fluid flow rate for liquid-solid systems results in a progressive expansion of the bed. A gas-fluidized bed does not expand uniformly with increasing fluid flow rate. Rather, bubbling of the gas is observed, and the bed does not expand much beyond its volume at minimum fluidization; this bed is referred to as a bubbling fluidized bed, a gas fluidized bed, or a dense phase fluidized bed. If the fluid velocity is increased further, the terminal velocity of the solid particles is exceeded, the upper surface of the bed disappears and the solids are carried out of the bed; this bed is known as a disperse, dilute or lean-phase bed.

As discussed in more detail later, the quality of fluidization affects the performance of the fluidized bed incinerator. In dense-phase fluidization, the gas is distributed between the bubble-phase and the emulsion-phase of the bed. The gas carried in the bubble-phase does not directly participate in the solid-gas reactions. However, the bubbles promote solids/solids and emulsion gas/solids mixing. Furthermore, in the gases in the bubble-phase and in the emulsion-phase are continuously exchanged as the bubbles rise through the bed. Several factors such as bed geometry, particle size, gas flow rate, gas distributor plate, and vessel internals affect the quality of fluidization. For example, a sintered distributor will give a better quality of fluidization than a single orifice plate because the sintered plate will produce many small bubbles wereas the single orifice plate will promote larger bubbles which leads to channeling and slugging. Better gas distribution is acquired at the cost of higher gas pressure losses, so that the design of the distributor plate is crucial in combining performance and economics. Despite identification of the factors involved in promoting a good quality of fluidization, no successful mathematical relationships have yet been developed which describe the effects of each factor on the quality of fluidization.

Recent efforts in mathematical modeling of fluidized beds have resulted in the predictions of their efficiency as chemical reactors rather than the definition of scale-up parameters. In developing these models various assumptions are made concerning bubble size and velocity, coalescence, gas velocity in the emulsion phase, particle size and shape, etc. So far, the relationship of these parameters with bed size is not established, so scale-up procedures are still based on previous experience.

Models predicting performance of fluidized beds are based on conditions more uniform and ideal than usually obtained operationally. Such factors as wall effects, distributor plate effects, number and location of waste feed points, etc., are rarely considered in developing hydrodynamic models of fluidized beds (although heat transfer to the walls has been modeled). For this reason, and because of transient upsets suffered in normal operations, models of "ideal" fluidized beds would most likely predict better efficiencies than are actually achieved.

Wastes contain combustible and noncombustible components and the combustible fraction is composed of volatiles and nonvolatiles. The volatiles are those compounds which volatilize at the relatively low operating temperatures achieved in the burning process in fluidized beds and are composed mostly of hydrocarbons. The nonvolatile combustibles are mostly carbonaceous and polymeric materials. The noncombustibles consist of moisture and inorganic ash, which influence the effluent concentrations and the behavior of the bed. They act as a thermal sink and thus can lower bed temperatures. Furthermore, some inorganics such as silicates and sodium compounds can defluidize the bed at high temperatures or appear in the effluent stream as flyash or metal oxides (see Section 2.3).

There are two sources of waste incineration inefficiency: (1) incomplete oxidation of the volatiles, and (2) loss of solids which contain unoxidized combustibles. In the design and operation of fluidized bed incinerators, the incomplete oxidation of solids presents the greater difficulty in attaining complete incineration because solids generally require a longer time for complete oxidation than gases at a specific temperature. Although the hydrodynamics of gas flow through a fluidized bed are extremely complicated, the residence time of vapors at a specific temperature, which can be calculated, basically determines the extent of oxidation of the volatiles. Computations of the extent of loss in solid form is more difficult. The loss of incompletely oxidized solids can occur by elutriation or by removal with the bed material. The bed material must be removed and regenerated, continuously or periodically, because of build-up of noncombustibles or attrition of the inert heat carrier (usually sand). Inadequate solid residence time is a major cause of inefficiency of fluidized bed incineration.

The efficiency of waste incineration in fluidized beds is influenced by several factors: (a) the physical form of the waste, (b) the chemical composition, and (c) the size of solid wastes. Furthermore, the performance of the incinerator, and hence, the prediction of effluents composition is dependent on factors such as inert particle size, temperature, feed mechanism, fluidizing air flow rate, size of the bed, etc., as well as on the kinetics of incineration. A complete model would involve the coupling of the kinetics of waste incineration with the factors which predict bed performance, and because neither is well understood, attempts to predict the composition of effluents from fluidized bed incinerators have not been successful.

Single particle models permit a first cut at analyzing the residence time requirement and/or determining what kind of waste preparation (shredding, crushing etc.) is needed. These models also yield some information for the evaluation of waste destruction efficiencies.

Several hydrodynamic models have been proposed, describing the gas interchange rate between the bubbles and the dense phase through which the bubbles rise. Correlations for solid particle attrition and elutriation of fines have also been proposed and will be discussed below.

3.3.1 Models of Oxidation of Single Particles

Fluidized bed reactors are, at present, designed on the basis of kinetic models for the oxidation of single particles, which determine the residence time needed complete combustion in the bed and in the freeboard. Three kinetic models[34] cover most cases:

The continuous reaction/constant size model is applicable to reactions in which a solid is consumed uniformly throughout the particle. The gas diffusion into the particle is much faster than the gas-solid reaction.

The unreacted core/constant size model (also known as the shell model) is applicable to cases where both or either the gas-solid reaction and the gas diffusion through the residual solid shell are controlling.

The shrinking particle model is applicable to the cases where oxidation leaves no solid residue, i.e., a case very similar to droplet combustion. Here either gas-through-gas diffusion or surface reaction can be controlling.

For the continuous reaction model, the progress of conversion of solid reactant B is independent of particle size as a first approximation (a uniform concentration of oxygen is implicit in the fast gas diffusion assumption). The rate of conversion of the solid reactant B is

$$\frac{dX_B}{dt} = K_V Ca \ (1-X_B)$$

where

X_B = fraction of B converted

C_A = concentration of oxygen (constant)

K_V = rate coefficient based on the volume of solid

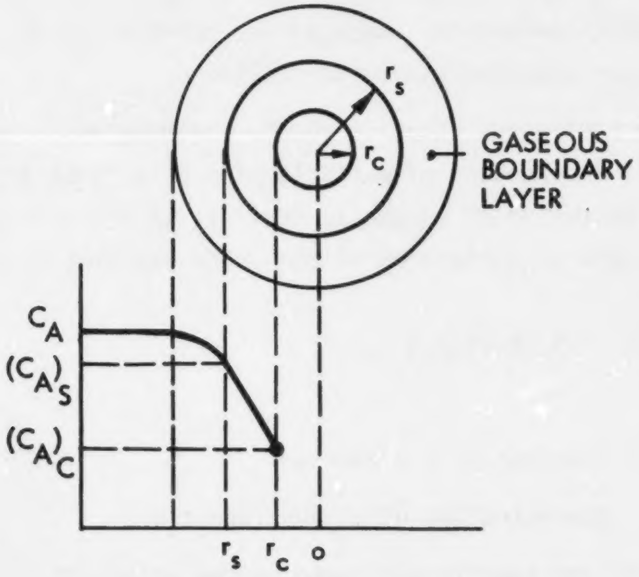
The continuous reaction model usually applies to very small particles. These are very likely to have been elutriated and at least part of the reaction is taking place in the freeboard. Note that the residence time required to completely oxidize the particle is independent of particle size.

The shrinking core/constant size model includes several mechanisms:

1. Oxygen diffuses through the boundary layer surrounding the particle to its surface.

2. Oxygen diffuses through the product layer to the reaction front.
3. Oxygen reacts with the solid in a narrow reaction zone.
4. Gaseous products diffuse to the main gas stream.

Figure 11 illustrates the diffusion of oxygen.



r_s
r_c
GASEOUS BOUNDARY LAYER
C_A
$(C_A)_S$
$(C_A)_C$
r_s
r_c
o

Figure 11. Shrinking core model.

In a vigorously bubbling bed, the diffusion resistances in steps 1 and 4 are not as great as the resistance in step 2 when there is a solid product layer. Consequently, either the reaction rate, the diffusion through the solid product layer (or a combination of the two) controls. Generally, when the reaction rate is strongly temperature-dependent, resistance to gas diffusion does not control the rate.

The chemical kinetics for heterogeneous oxidation of a spherical particle are represented as first-order in oxidant[34]. Thus, for an unreacted core of radius r_c, the rate of reaction of A (oxygen) is represented as:

$$-\frac{dN_A}{dt} = 4\pi \, r_c^2 \, K \, (C_A)_c \qquad (1)$$

where

N_A = moles of oxygen
t = time
r_c = radius of particle at the reaction zone
K = kinetic rate constant (first-order irreversible reaction)
$(C_A)_c$ = concentration of oxygen at r_c

The rate equation for the disappearance of A due to diffusion through the solid product layer is:

$$-\frac{dN_A}{dt} = 4\pi \, r_c^2 \, De \, \left(\frac{dC_A}{dr}\right)_{r_c} \qquad (2)$$

where

De = effective diffusivity of oxygen through the solid product layer

A steady-state concentration gradient through the product layer leads to a mass balance such that

$$\frac{d}{dr}\left(r^2 \, De \, \frac{dC_A}{dr}\right) = 0 \qquad (3)$$

The expression is integrated twice with the boundary conditions:

$C_A = (C_A)_s$ at $r = r_s$

$C_A = (C_A)_c$ at $r = r_c$

where

r_s = radius of spherical particle

$$\frac{C_A - (C_A)_c}{(C_A)_s - (C_A)_c} = \frac{1 - r_c/r}{1 - r_c/r_s} \quad . \qquad (4)$$

so,

$$\left(\frac{dC_A}{dr}\right)_{r_c} = \frac{(C_A)_s - (C_A)_c}{r_c\,(1 - r_c/r_s)} \qquad (5)$$

Substituting equation (5) into equation (2) gives

$$-\frac{dN_A}{dt} = 4\pi\, r_c\, De\, \frac{(C_A)_s - (C_A)_c}{1 - r_c/r_s} \qquad (6)$$

$-\frac{dN_A}{dt}$ can be eliminated from equation (1) to yield a value for $(C_A)_c$ in terms of $(C_A)_s$:

$$(C_A)_c = (C_A)_s[1 + \frac{r_cK}{De}\ (1 - r_c/r_s)]^{-1} \qquad (7)$$

Substituting equation (7) into equation (1) yields

$$-\frac{dN_A}{dt} = 4\pi\, r_c^{\,2}K(C_A)_s[1 + \frac{r_cK}{De}\ (1 - r_c/r_s)]^{-1} \qquad (8)$$

According to the spherical geometry of the particle, the time rate of disappearance of the particle is:

$$-\frac{dN_B}{dt} = -\frac{\rho_B}{M_B}\ \frac{d}{dr}\,(\frac{4}{3}\,\pi\, r_c^{\,3}) \qquad (9)$$

where

N_B = moles of particle B
ρ_B = density of B
M_B = molecular weight of B

Thus,

$$\frac{dN_B}{dt} = \frac{4\pi \; r_c^{\,2} \rho_B}{M_B} \; \frac{dr_c}{dt}$$

The stoichiometry is such that

$$\frac{dN_A}{dt} = \frac{1}{b} \; \frac{dN_B}{dt} = \frac{4\pi \; r_c^{\,2} \; \rho_B}{bM_B} \; \frac{dr_c}{dt} \qquad (10)$$

where b = stoichiometric constant.

Thus,

$$\frac{dr_c}{dt} = \frac{bM_B K(C_A)_s}{\rho_B} \left[1 + \frac{r_s K}{De} \; \frac{r_c}{r_s} \left(1 - \frac{r_c}{r_s}\right)\right]^{-1} \qquad (11)$$

Thus, the time rate of particle shrinkage can be evaluated if $(C_A)_s$ is known. For fluidized bed incinerators operating with excess O_2, the assumption of $(C_A)_s$ as constant and equal to the mean oxygen concentration is reasonable.

Equation (11) can be integrated to yield the time necessary for a particle to completely disappear. For cases where both the reaction kinetics and diffusion through the product layer represent rate limiting steps, Equation (11) must be solved using numerical methods. When either the chemical kinetics or diffusion controls the rate of reaction, an analytical solution is possible.

Kinetic controlled: $r_s K << De$

$$\frac{dr_c}{dt} = + \frac{bM_B \; K \; (C_A)_s}{\rho_B}$$

so,

$$t = \frac{\rho_B r_c}{bM_B \; K \; (C_A)_s} \tag{12}$$

i.e., the residence time needed to completely react a particle is proportional to the particle radius.

Diffusion control case: $r_s K >> De$

$$\frac{dr_c}{dt} = \frac{bM_B \; (C_A)_s \; De}{\rho_B \; r_c} \quad \frac{r_s}{r_s - r_c}$$

$$t \cong \frac{\rho_B r_c^{\;2}}{2bM_B \; (C_A)_s \; De} \tag{13}$$

In this case the residence time for complete particle oxidation is proportional to the particle radius squared.

The shrinking particle model is very similar to the model for liquid fuel drop burning discussed in Section 4.2.3, and differs from the unreacted core only in that the controlling diffusion rate is now that of the oxygen diffusing through a gas layer. For small particles, at temperatures below 1300 K, the reaction rates are low, and are controlling. Equation (1) is applicable, with r_c representing the ever diminishing radius of the particle. The time needed to consume a particle is given by equation (12) when the reaction rate is low. When gas diffusion is controlling (highly reactive solids) equations (13) applies, with the diffusion coefficient De representing diffusion of oxygen through the gaseous boundary layer rather than thru the spend solid layer.

3.3.2 Hydrodynamic Models

The fluid mechanical properties of the bed have important consequences on the attrition, elutriation, and the gas interchange between phases. Efforts in modeling fluidized beds have usually accepted the two-phase model first proposed by Toomey and Johnstone[35]: a bubble phase in which the gases, essentially free from solids, rise through the bed and a dense phase consisting of both solids and gas. Bubbles form at an unpredictable rate, grow, coalesce and may even split. There is clearly a gas flow through the bubbles, so that there is gas interchange between the phases. Particles move up and down and around the bubbles, and some rise in the wake of each bubble.

Several hydrodynamic models have been proposed and they were reviewed by Horio and Wen[36]. A number of assumptions must be made in specifying a model such as uniform bubble size, uniform void fraction, etc.

Horio and Wen worked out a code to classify fluidized-bed reactor models including a system that classifies the assumptions and factors included in the model; they also classify the models by levels of sophistication. But, to quote Horio and Wen[36], "Inspite of the many improvements attempted by many researchers, the accuracy of the fluidized bed reactor models is still insufficient for general use in design and scale-up."

3.3.3 Attrition and Elutriation

Attrition and elutriation have been modeled by Merrick and Highley[37] based on data obtained in a fluidized bed coal combustion plant. They developed a new form of correlation for the elutriation, superseding the widely used Wen and Hashinger correlation which exhibits improper behavior for small particles (see Reference 34 p. 316 for this correlation). It remains to be seen if the work Merrick and Highley is applicable to waste incinerators with sand beds with very different particle size distribution and reaction kinetics than those describing pulverized coal in a bed of limestone.

3.3.4 Effluent Prediction

Pollutants can arise from three sources in fluidized bed incineration: (1) elutriation, (2) continuous or periodic removal of bed material containing uncombusted wastes, and (3) gaseous hydrocarbon emissions.

First, elutriation is considered and the following assumptions are used to develop the model:

1) There is a critical size, r_c, such that particles smaller than this size are elutriated to the freeboard immediately from the bed. Merrick and Highley[37] present a correlation showing that $r_c \leq 1.6 r_t$ where r_t is the size particle whose

terminal velocity is equal to the fluidizing velocity U_f. Consequently, r_c, and hence the amount of bed material elutriated is dependent on the operating conditions of the bed (because the larger r_c, the larger proportion of bed material that is finer than the critical size). The well-known expression for terminal velocity is:

$$U_t = \frac{4g\,(\rho_p - \rho_g)\,d_p}{3\rho_g C_D}$$

where

U_t = terminal velocity, m/s.
g = gravitational acceleration, m/s^2.
ρ_p = density of particle, kg/m^3.
ρ_g = density of fluid, kg/m^3.
d_p = particle diameter, m.
C_D = drag coefficient, dimensionless.

Of course, the drag coefficient is dependent on the Reynolds number and the shape of the particle.

2) Particles which are larger than r_c stay in the bed until they are reduced to a size smaller than the critical radius by simultaneous attrition and chemical reaction. They are then elutriated to the freeboard.

3) As the particles rise through the freeboard, they may be further reduced in size by combustion. It is assumed that the rate of reaction is controlled by diffusion such that the time for complete conversion is

$$t_i = \frac{D_o^2}{K}$$

where

t_i = time needed for incineration, s.
D_o = diameter of particle, m.
K = effective diffusion rate constant, m^2/s.

4) No attrition, abrasion, or agglomeration occurs in the freeboard.

5) Upward particle velocity is assumed to be $(U_f - U_t)$. Although U_t decreases with decreasing size at low Reynolds numbers, the velocity change due to decreasing size is small when compared to the overall velocity. Hence, the particle's upward velocity is assumed to be constant. Consequently,

$$t_f = \frac{L}{(U_f - U_t)}$$

where

t_f = residence time in the freeboard, s.
L = height of freeboard, m.
U_f = fluidizing velocity, m/s.
U_t = terminal velocity, m/s.

Small size combustible particles which are elutriated to the freeboard will burn sufficiently quickly such that they are not carried out of the freeboard. Consequently, for a given particle size distribution in the bed, only a narrow cut of particles will be elutriated as shown in Figure 12.

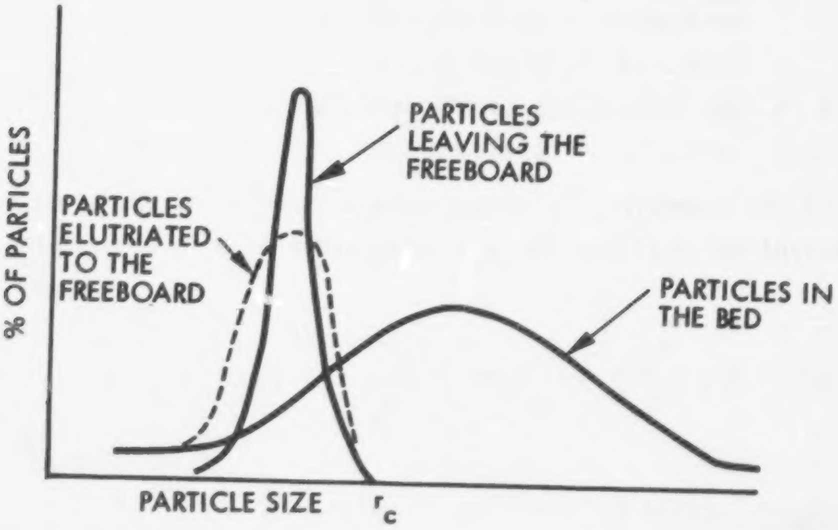


Figure 12. Particle elutriation.

The larger sized particles are not elutriated to the freeboard, giving the narrow cut of elutriated material.

Incompletely Oxidized Vapors--

Unburned hydrocarbons and CO are effluents which are indicative of incomplete oxidation of the vaporized material. Although mixing in the bed is generally adequate for complete oxidation, some hydrocarbon vapors are generated near the top of the bed and swept to the freeboard before oxidation is completed. Furthermore, bubbles which are lean in oxygen will contain unburned hydrocarbons. Although the gas interchange coefficient describes the rate of gaseous interchange between the bubbles and emulsion gas, the residence time of a particular bubble depends on its place of origin in the bed. Assuming that all bubbles originate near the distributor plate, and the bubbles have a velocity on the order of the gas velocity near the distributor plate or that the bubble velocity can be determined experimentally, then

$$I = \frac{L\,K}{U_b}$$

where

I = the number of times that the bubble is completely replaced with emulsion gas.

L = height of fluidized bed, m.

K = gas interchange coefficient, s^{-1}

U_b = velocity of bubble, m/s.

Kunii and Levenspiel[34] have proposed a correlation for a gas interchange rate constant which allows for gas interchange by both convection and diffusion.

$$K = 4.5 \left[\frac{U_{MF}}{d_b}\right] + 5.85 \left[\frac{D_g^{1/2}\, g^{1/4}}{d_b^{5/4}}\right]$$

where

U_{MF} = minimum fluidizing velocity, cm/s.

d_b = diameter of bubble, cm.

D_g = gas diffusion coefficient, cm^2/s.

g = gravitational acceleration, cm/s^2.

A high value of I means that the gas between the bubble and emulsion has interchanged many times, and hence the mixing is good. However, a correlation between I and incineration efficiency has yet to be formulated.

Unreacted vapors entering the freeboard will have additional time to react with oxygen. The oxidation completness depends on the mean residence time in the freeboard (i.e., flow rates and freeboard height) and on the turbulence level in the flow; thus the conditions are similar to those encountered in by vapors in liquid injection incinerators beyond the flame zone.

3.3.5 Summary

Despite intensive efforts to analyze, correlate and model the hydrodynamic, heat and mass transfer and the reaction mechanisms in fluidized bed reactors, there are today no scaling laws and very few proved design and operating parameters which would permit the evaluation of the hazardous waste destruction capability of a proposed fluidized bed reactor.

3.4 MULTIPLE HEARTH INCINERATORS

Multiple hearth furnaces are particularly well suited for the incineration of solid wastes and sludges. A cross section of a multiple hearth incinerator is shown in Figure 13. The wastes are fed to the top hearth while air is fed to the bottom hearth. A shaft which is positioned vertically through the furnace swings the arms across each hearth. The angle of the rabble teeth on the arms determines whether the solid material moves outward or inward across the hearth. The waste material which spirals inward on the hearth drops through a hole in the center of the hearth, while the material which spirals outward passes through a series of drop holes on the circumference of the hearth. The hearths are arranged vertically with alternating in-hearths and out-hearths. The flow of solid material through the reactor can be controlled by the rotational speed of the shaft, the spacing of the rabble teeth, and the distance between the bottom of the teeth and the hearth.

The kinetics of solid waste incineration are described in the fluidized bed section. The proper residence time for complete sludge or solid incineration must be determined experimentally. Then various operating parameters

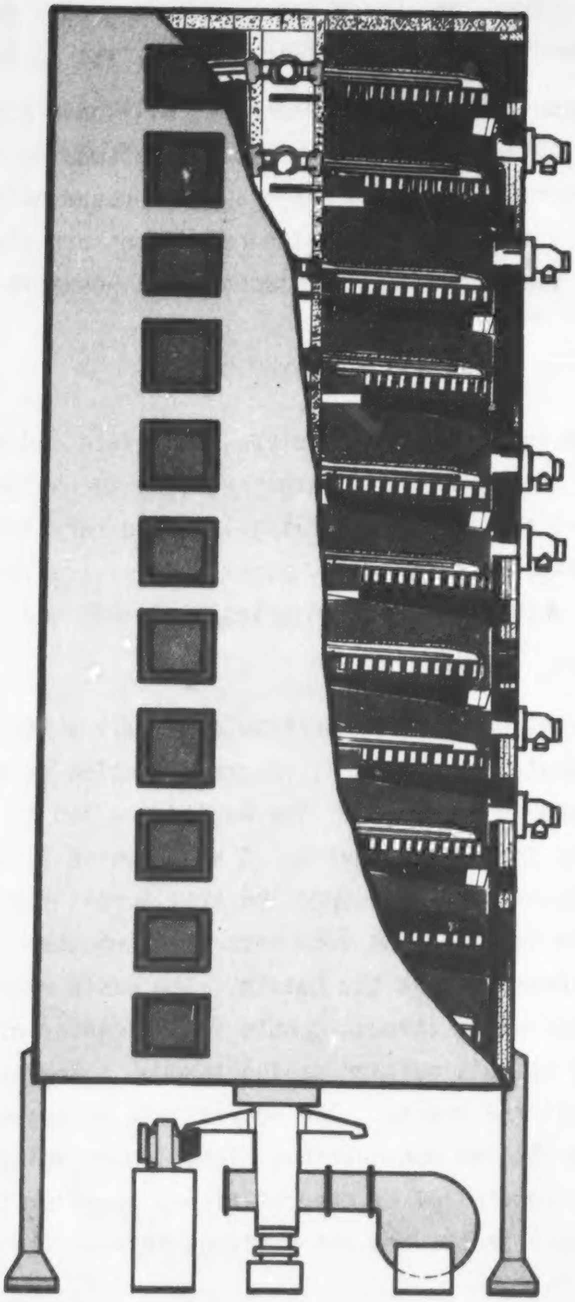


Figure 13. Multiple hearth cross section.

such as feed rate, shaft rotational speed, and the spacing, angle and size of the rabble teeth, can be adjusted to the particular incineration requirements.

The multiple hearth incinerator is characterized by different zones, each comprised of one or more hearths. The waste is fed near the top of the reactor where any water associated with the waste is driven off. This top zone is termed the "drying zone". Some multiple hearth furnaces have a hearth above the drying zone hearths which serves as an afterburner. The waste is fed to the drying zone, while air is fed to the afterburner to facilitate the oxidation of unburned CO hydrocarbons and vapors. Below the drying zone is the combustion zone. Air is fed to the bottom of the combustion zone while the solids fall into it from the drying zone. Below the combustion zone is the ash cooling zone through which the ash drops before removal from the furnace.

3.4.1 Temperature Profiles

The temperature profile is such that the temperature drops through each hearth as the gas rises from hearth to hearth. The temperature in the afterburner, however, may be higher than the temperature in the drying zone. Typically, the temperature is controlled by using excess air or auxiliary fuel which are both fed at the bottom of the combustion zone.

A typical temperature profile is sketched in Figure 14.

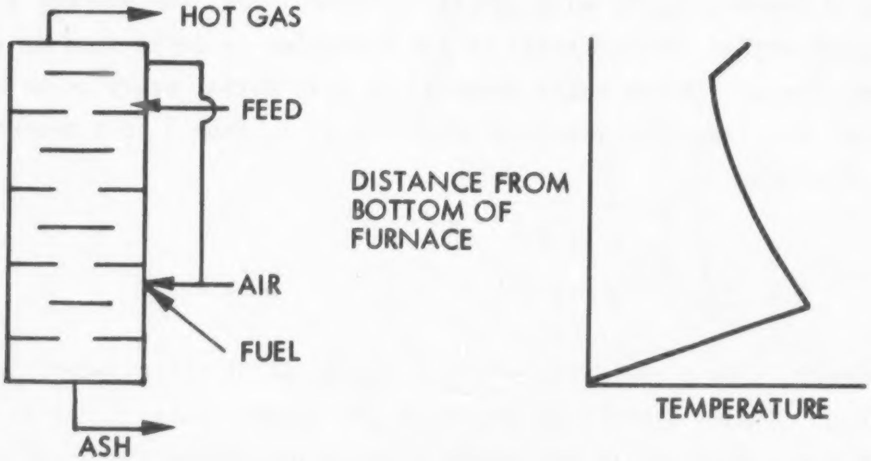


Figure 14. Temperature profile in a multiple hearth incinerator.

The use of either excess air or auxiliary fuel shifts the temperature profile to the left or right respectively from the profile derived from the incineration of feed without the use of excess air or auxiliary fuel. The temperature difference across each hearth is dependent on such factors as gas flow, the solid mass in each hearth, and the furnace's heat release

3.4.2 Turbulence and Mixing

The gas turbulence in the furnace is difficult to characterize. The design of the furnace is such that the gas travels from the inside of one hearth to the outside of the next hearth. Turbulence is promoted by the countercurrent contacting of the gas with the solid waste as the gas rises through the dropholes. There is no satisfactory model to predict the degree of turbulence from the various operating parameters.

The mixing of solids in the furnace is also difficult to characterize a priori. Mixing occurs as the solid waste drops through a center drophole in an "in-flow" hearth. The degree of mixing can be defined using experimental data, and is usually described in statistical terms. Various analytical methods such as gravimetric, volumetric, electrometric, particle counts, and optical have been used to describe the degree of mixing. A general procedure for determining the degree of mixing is to add a tracer material to the waste material. Let μ be the fraction of tracer in the waste. A number, N, of small samples are taken from various locations in the multiple hearth and the fraction of tracer, X_i, in each sample is determined. The average value of the measured tracer concentration in the N samples is designated by $\bar{X}$. As N increases, $\bar{X} \rightarrow \mu$. If the waste material is well mixed, every value of X_i would equal $\bar{X}$. Thus, the standard deviation of X_i from $\bar{X}$ is a measure of the quality of mixing.

$$S = \sqrt{\frac{\sum_{i=1}^{N} (X_i - \bar{X})^2}{N - 1}}$$

However, S is a valid measure only for a set of tests under specific conditions. A more general parameter is the mixing index, I. I is the ratio of S/σ_0, where σ_0 is the standard deviation before the onset of mixing. Smith and Van Ness[38] propose the equation

$$\sigma_o = \sqrt{\mu (1 - \mu)}$$

Thus,

$$I = \frac{S}{\sigma_o} = \sqrt{\frac{\sum_{i=1}^{N} (X_i - \bar{X})^2}{(N - 1) \mu (1 - \mu)}}$$

In a batch mixing process, I is unity before mixing begins and becomes progressively smaller. Theoretically, I would approach zero at long mixing times, but mixing is never complete and analytical methods are not precise enough to give measured values of X_i equal to each other. Typically the low values of I fall in a range of 0.1 to 0.01.

3.4.3 Residence Time of Gases and Solids

The simplest method for determining the residence time of the gas phase is to assume plug flow through the incinerator. Thus,

$$t = \frac{V}{W}$$

where

t = residence time.

V = volume of multiple hearth incinerator.

W = volumetric flow rate of air.

Vapors which are generated from the solid wastes are assumed to be swept through the multiple hearth incinerator at the same flow rate as the air fed to the incinerator. Therefore, the residence time of vapor generated in a given hearth will depend on the vertical location of that hearth.

As mentioned previously, the solid waste moves across each hearth in a spiral. The expression describing the movement of the solid material across the hearth in polar coordinates is:

$$r = \pm a \theta$$

where

r = Distance from center of the hearth.

a = Distance of teeth from the center of hearth. (Assuming they are evenly spaced)

θ = Angle

$\pm$ = Describes whether the material is moving towards or away from the center of the hearth (+ for an "out-hearth"; - for an "in-hearth")

If r = radius of hearth and $\dot{\theta}_2$ = angular velocity, then the time for the solid to traverse across the hearth, t, is:

$$t = \frac{r}{E a \dot{\theta}_2}$$

here E is a factor describing the slip of solid matter with respect to the movement of the rake teeth. For liquid wastes E depends on viscosity and can be estimated. For solid wastes the slippage depends on several factors such as size, shape, and moisture content of the material and is less readily estimated. The height of the dead-bed, which is the height of material on each hearth, also affects the slippage of material. The slippage of material is greater the further the material is from the rake teeth such that the material on the floor of the hearth moves across the hearth more slowly than the material closer to the rake teeth.

3.4.4 Scale-up Parameters

Scale-up of rotating hearth incinerators will be limited by the necessity of keeping angular velocity low, so as not to increase velocity of the outermost rake teeth beyond acceptable values. The relationship between incinerator capacity and hearth diameter, incinerator height and rotational speed is complicated by the dependence of solids and gas residence times not only on incinerator height and diameter but also on the rake teeth configuration (angle, spacing etc.) and the properties of the solids. The probability of developing useful generalized scaling laws for multiple hearth incinerators is not high.

3.4.5 Summary

Multiple hearth incinerators are widely used for waste incineration. Nevertheless, there seems to have been very little effort made to develop an analytical basis for the design of these furnaces. The development of a general treatment, i.e., one applicable to a wide range of wastes, would involve the expenditure of much effort - including the collection of data (temperatures, gas and solids compositions) and the development of solids mixing - rabble teeth geometry correlations.

3.5 ROTARY KILN INCINERATORS

Rotary kiln incinerators are long, cylindrical rotating furnaces in which solids and slurries are heated by combustion of an auxiliary fuel. The fuel, as well as the solids can contain hazardous components. The axis of the kiln makes an angle with the horizontal. The feed is introduced at the upper end of the kiln and the hot product discharged at the lower end. Fuel and air inlets are located either at the lower end, resulting in a countercurrent gas/solids flow, or in the upper end, yielding a cocurrent flow. The rotation of the kiln provides continuous mixing of the solids and continuously renewed contacts between solids and the hot walls as well as direct contact with the hot gases. Exposure to hot gas is often enhanced by the use of hanging chains, which break up any solid chunks, mix and stir slurries and permit wet, sticky material to cling to the chains until dry. In direct fired kilns, the solid materials are not showered through the gas stream, as they are in dryers, but are retained in the lower part of cylinder, except in the feed section in which the hanging chains (if any) do lift the material into the gas stream.

Often the kiln is preceeded by drying or preheating installation such as moving grates, and is followed by an afterburner. The effect of these devices on hazardous waste destruction must, of course, be accounted for when examining the thermal decomposition of hazardous wastes in the incineration facility. Here we will address only the process taking place in the rotary kiln itself.

3.5.1 Combustion and Heat and Mass Transfer

Rotary kiln incinerators are heated by natural gas, oil or pulverized coal. The kilns are usually very long, so that the combustion zone occupies a small portion of the incinerator. Most of the heating of the charge is due to exchange with the combustion product gases and the walls of the kiln. Mass transfer, drying and volatilization of the charge, is very important in the case of solid or liquid waste incineration, but only drying has been analyzed in the literature. Moreover, the correlations for drying of the charge pertain to low temperature rotary driers with "flights", i.e., scoops on the walls of the kiln; these scoops scoop up the charge and shower it through the combustion gas so that the charge receives heat by direct contact with the gases. The correlations for rotary dryers are of the form

$$Q_{ch} = Ua\ v\ (\Delta T)_m$$

Q_{ch} = heat transferred to the charge (J/s)
Ua = volumetric heat transfer coefficient ($J/s \cdot K \cdot m^3$)

v = dryer volume (m^3)

$(\Delta T)_m$ = mean temperature difference between charge material and hot gases (K)

A correlation for the volumetric heat transfer coefficient has been developed. It is of the form

$$Ua = KG^n/D$$

where D is the kiln diameter and G is the mass flowrate of the combustion gas ($kg/s\text{-}m^2$ of kiln cross section).

P. Y. Mc Cormick[39] has correlated data for single shell direct heat dryers; he found that

$$n = 0.67$$

and proposed that, in order to segregate independent design parameters, the correlation should take the form

$$Q_{ch} = bLDG^n\ (\Delta T)_m\ f_1(N_f) f_2(M)\ f_3(A)\ f_4(N)$$

where b is a proportionality constant, L and D the length and the diameter of the kiln, and f_1, f_2, f_3 and f_4 functions of the number of flights N_f, the radial flight depth M, the flight load A, and the rotation speed of the kiln N, respectively. Note that direct radiative heating from flame and walls, and direct wall contact heating are not represented, which is justified in the relatively low temperature rotary dryer applications, but not for incinerators. The heat exchange mechanisms in the latter are too intricate to allow for simple correlations, and a more sophisticated approach e.g., model development is needed.

The mathematical treatment of high temperature rotary kilns found in the literature is limited to specific applications, such as cement kilns or ore dryers and do not lend themselves to generalization. Exceptions are a model presented by Sass[40] which includes a preheat section wherein the solids are heated to the boiling point of the liquid, and an isothermal section where the liquid is evaporated, followed by a final section where the solids are heated to a desired discharge temperature; and a very useful treatment by Imber and Pashkis[41] in which dimensionless parameters were used. A schematic diagram of the heat flow paths in a cross-section of a rotary kiln is shown in Figure 15 taken from the work of Imber and Pashkis. Sass includes some heat loss to the ambient air. The heat transfer equations from gas to kiln wall to the charge used by Sass (Reference 40) are shown in Table 8, taken from that reference.

The most salient feature of these equation is the use of the emprical correlation

$$h = 0.05\ (C_g/S_x)^{0.67}$$

for gas-to-wall heat transfer and

$$h = 0.25\ (C_g/S_x)^{0.67}$$

for the corresponding wall to charge heat transfer. These correlations are at best applicable as a rule of thumb, useful to calculate an approximate kiln length.

Solids and gas emissivity calculations also present some difficulties, because of gas-borne particle radiation and uncertainties of the emissivities of solids in the charge. If and when better documented heat and mass transfer correlations are developed, an analytical treatment of the heat transfer in

TABLE 8. HEAT-TRANSFER COEFFICIENT CORRELATIONS

Heat-transfer path	h_i
Gas to inner kiln wall	$h_1 = 0.05\ (G_g/S_x)^{0.67} + 0.173 \times 10^{-8}\ E_g(T_g^4 - T_w^4)/(T_g - T_w)$
Gas to solid	$h_2 = 0.05\ (G_g/S_x)^{0.67} + 0.173 \times 10^{-8}\ E_g(T_g^4 - T_s^4)/(T_g - T_s)$
Inner kiln wall to solid	$h_3 = h_{3cc} + h_{3RAD}$ $h_{3cc} = 0.25\ (G_g/S_x)^{0.67}$ $h_{3RAD} = 0.173 \times 10^{-8}\ fE_s(T_w^4 - T_s^4)/(T_w - T_s)$
Inner kiln wall to outer kiln wall	$h_4 = \dfrac{k}{r_o - r_i}$
Outer kiln wall to ambient air	$h_5 \approx 2.5$*

*Approximate value used to obtain initial estimate of outer-wall temperature. With this estimate, a more accurate value of h_5 was computed.

D_i = inner kiln diameter
E_g = gas emissivity
E_s = solid emissivity
f = correction factor
k = thermal conductivity of insulating brick
S_x = cross-sectional area of kiln
θ = fill angle as shown in Figure 15
T_s = solid temperature
T_g = gas temperature
G_g = mass flow rate of wet gas
G_s = mass flow rate of wet solid

the rotary kiln incinerator (and hence a good basis for scale-up) will become possible because the problem is then reduced to solving a periodic heat conduction problem which is defined by classical non-dimensional parameters: a Fourier number and two Biot numbers, as discussed below.

3.5.2 Non-dimensional Parameters

Heat is received from the gases by the kiln wall, and transported to the charge. If we follow an element $rd\theta$ of the kiln wall from the position marked "origin" on Figure 15, as it emerges from contact with the charge and is rotated through the ange $(2\pi-\theta_0)$, that wall element will be progressively heated by the combustion gases. Initially the temperature distribution in that element was $T_0(r)$, after a rotation of $(2\pi-\theta_0)$, i.e., after a time period of $(2\pi-\theta_0)/2\pi N$ seconds (N is the number of revolutions per second), the temperature distribution in the element is $T_1(r)$. Neglecting axial conduction, the equations describing the heat transfer are:

$$\frac{\partial T}{\partial t} = \alpha\nabla^2 T = \alpha\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\ \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial \theta^2}\right)$$

$$\frac{\partial T}{\partial r} = h_1(T_g-T), \qquad r = r_i$$

$$T = T_0(r,\theta), \qquad t = o$$

where α is the the thermal diffusivity of the brick. If $(\partial^2 T/\partial\theta^2)$ is small compared to the radial derivatives, the solutions will be of the form

$$\frac{T-T_g}{T_o-T_g} = f(Fo,\ Bi)$$

where Fo is the Fourier number $Fo = \alpha t/\bar{r}^2$ and Bi is the Biot number $Bi = h_1\bar{r}/k$. Closed form solutions are cumbersome and require simplifying assumptions because radiation causes the heat transfer coefficient to depend on temperature*.

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*Imber and Paschkis (Reference 41) give closed form solutions for two limiting cases.

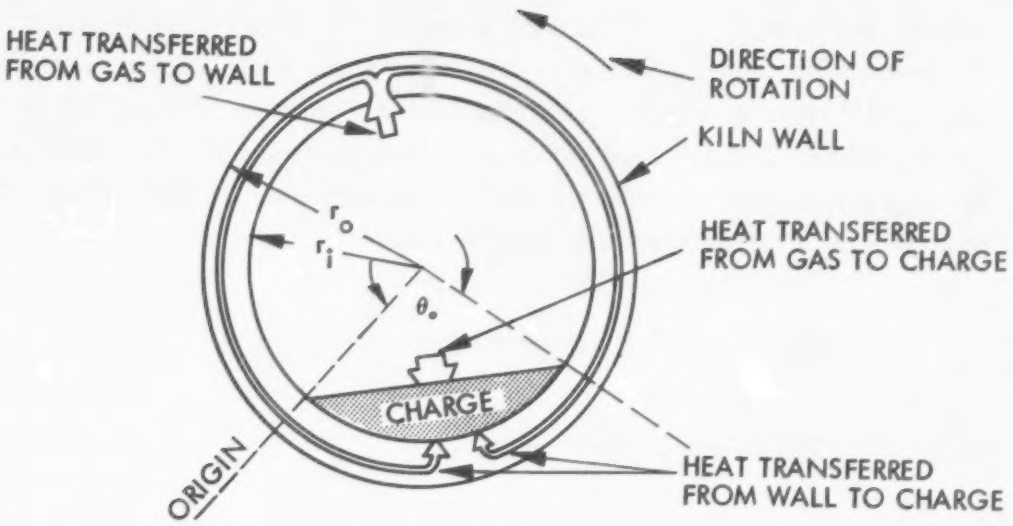
HEAT TRANSFERRED FROM GAS TO WALL
DIRECTION OF ROTATION
KILN WALL
r_o
r_i
θ_o
HEAT TRANSFERRED FROM GAS TO CHARGE
CHARGE
ORIGIN
HEAT TRANSFERRED FROM WALL TO CHARGE

Figure 15. Schematic diagram showing the heat-flow paths and Nomenclature for a typical section in a rotary kiln.

Numerical solutions are quite readily accessible. At the end of the time period $(2\pi-\theta_0)/2\pi N$, the kiln wall element, $\bar{r}d\theta$, which we are following, reaches the upper border of the charge. The temperature distribution in the element is known, and heat is transferred from the element to the (cooler) charge. The equations for the wall in contact with the charge is:

$$\frac{\partial T}{\partial t} = \alpha\nabla^2 T$$

$$\frac{\partial T}{\partial r} = h_s(T-T_s), \quad r = r_i$$

$$T = T(Fo_1, Bi_s), \quad t = \frac{1}{N}\;\frac{2\pi-\theta_0}{2\pi}$$

where

$$Fo_1 = (\alpha/\bar{r}_i^{\,2})[(2\pi-\theta)/2\pi N] \qquad Bi_s = h_s\bar{r}/h_s$$

A steady state will be reached when the temperature distribution after one whole revolution is the same as the assumed initial distribution To(r).

The steady state solution depends on one Fourier number, $\alpha(2\pi-\theta_0)/2\pi N\bar{r}^2$ and on two Biot numbers - $h_1\bar{r}/k$ and $h_s\bar{r}/k$. The heat transfer coefficient h_1 must include gas and particulate (dust) radiation and convection. Gas radiation, mainly due to carbon dioxide and water vapor, can be readily calculated (Reference 15); particulate radiation is less accessible since dust loading and dust size distribuiton inside the kilns are hard to measure. The convective transfer can be described by conventional Nusselt, Reynolds, Prandtl number correlations. The heat transfer to the solids is less well defined and must generally account for all three heat transfer mechanisms. Furthermore, direct heat flow from gas to charge must be accounted for.

Mass transfer and/or chemical reactions were not included here, and these mechanisms will introduce another set of parameters which will influence the destruction of hazardous components.

3.5.3 Residence Time of Gases and Solids

In the above analytical approach we have neglected the progress of the charge from the inlet to the exit of the kiln, i.e., the residence time of solids, which depends on the slope of the rotary kiln axis and on the varying friction-related properties of the charge. The latter seem to have little influence since the empirical correlation for "time of passage" given in Perry's Handbook does not include charge properties:

$$\theta = 0.19(L/D)/(SN) \text{ (min.)}$$

where

L, D = kiln length and diameter
s = slope of kiln (m/m)
N = RPM

Evaluation of the residence time of combustion gases of the auxiliary fuel is straightforward, that of gases evolving from the charge more difficult. Mass transfer from the charge to gas stream will have to be addressed, as well as the chemical reactions in the charge and in the gases.

3.5.4 Scale-up Parameters

Despite all the uncertainties and gaps in the definitions of heat and mass transfer, limited scale-up of existing kilns can be undertaken by attempting to keep the values of the Fourier, Biot and Reynolds numbers unchanged or as close as possible. The limiting assumptions are that the heat and mass transfer coefficients will not change greatly because of scale-up, that an increase in charge depth will not drastically change its behavior (particle size in the charge will not scale-up, but the height will, hence charge mixing may change), and that the rotational speed decrease needed to limit stress levels will not impair heat transport.

3.5.5 Summary

Rotary kiln incinerators are the most versatile of all devices for hazardous waste incineration. Mathematical examination of the processes within the kiln does not present insurmountable difficulties; however, a sufficient experimental basis is not available at present. A concerted effort towards the development of an experimental basis and of an analytical description of the thermochemical phenomena in the rotary kilns should be undertaken.

SECTION 4

THERMOCHEMICAL AND KINETIC CHARACTERIZATION OF WASTES

Temperature - residence time relationships obtained in the laboratory have been the basis for establishing the requirements for the thermal destruction of hazardous wastes. The University of Dayton Research Institute has developed a special laboratory technique, incorporating a two stage quartz system, which was successfully used to determine the thermal decomposition properties of polychlorinated biphenyls (PCB's) and of Kepones[42,43] and permitted the selection of the appropriate incineration systems and of their operating conditions to safely dispose of the highly toxic wastes containing Kepones or PCB's.

In this system the pesticide was first converted to the gas phase, then exposed to the high-temperature destruction conditions. Critical parameters of temperature and residence time were accurately measured. Thermal destruction testing was conducted with three pesticides: Kepone, Mirex, and DDT. Both the Kepone and DDT molecules, at a residence time of ∿1 second, were essentially destroyed at 500°C; however, Mirex, at the same residence time, required 700°C for destruction. The thermal destruction properties of PBC's and related compounds were similarly determined. Initial decomposition occurred at about 640°C; 99.995% molecular destruction was found at 1000°C. Also, it was determined that PCB's (and certain related compounds) thermally decompose to low molecular weight products. An extension of the above technique to include thermal destruction in the presence of oxygen is being planned and should be very valuable.

The experimental techniques are essential and irreplaceable. However, the effort and time involved in conducting the experiments are substantial and can be greatly assisted by also conducting a thermochemical kinetic analysis of the combustion of the wastes in air. Equilibrium analysis cannot eliminate the need for the experimentally acquired reaction rate information on some of the hazardous compounds, but can serve to decrease the number of experiments required and provide essential information on the formation of dangerous intermediate products.

TRW has developed a method for examining the combustion of pesticides and other organic compounds by determining the equilibrium product distribution under various operating conditions[44]. A way to analytically determine the upper limit for the residence time required was also developed during pesticide incineration tests. It was based on the finding that the slowest and controlling step in high temperature combustion is the oxidation of the initially formed carbon monoxide.

The following sections describe the TRW approach to the thermal equilibrium and kinetic analysis for pesticide incineration.

4.1 THERMOCHEMICAL ANALYSIS

4.1.1 TRW Chemical Analysis Program

Determination of the theoretically expected equilibrium products of pesticide combustion requires appropriate thermochemical data for each potential product. In addition, a mathematical model is required to combine these data in order to ascertain the equilibrium quantities of each product. The data and model are used under various conditions of temperature, pressure, and reactant combinations to simulate each chemical system and reaction stage.

The primary data base used by the TRW Chemical Analysis Program included the JANAF thermochemical tables prepared by the Dow Chemical Corporation and a previous TRW effort to characterize the equilibrium product distribution of waste plastics combustion/pyrolysis. The JANAF tables include the potential products methane, acetylene, ethylene, ethylene oxide, formaldehyde, and the various methyl chlorides among the organics; but no higher organics are represented. The TRW addition include data for the following classes of compounds:

Higher saturates, e.g., alkanes
Higher unsaturates, e.g., alkenes
Alcohols

Glycols
Higher aldehydes
Ketones
Ethers
High Aliphatic chlorides
Amines
High expoxides
Aromatics
Alicyclics, e.g., cyclopentadiene
Polynuclear aromatics, e.g., naphthalene
Organic acids, e.g., acetic acid
Chlorinated aldehydes, e.g., chloral
Chlorinated aromatics, e.g., chlorobenzenes and chlorophenols
Chlorinated alicyclics, e.g., hexachlorocylopentadiene.

4.1.2 Equilibrium Product Distribution Analyses

The purpose of the equilibrium product distribution analyses is to provide a sound thermochemical basis for the determination of the species resulting from the combustion or pyrolysis of a hazardous waste. For example, in the combustion studies, for pesticide incineration the equilibrium product distributions were examined for the temperature range 800 K (1000 F) to 1650 K (2500 F) and for three air/fuel ratios:

Case 1: Stoichiometric amount of air
Case 2: 130 percent of stoichiometric amount of air
Case 3: 70 percent of stoichiometric amount of air.

In the pyrolysis studies, the thermochemical computer program was applied to determine not only the equilibrium product distribution, but also the secondary thermodynamically feasible reaction products. This was accomplished simply by eliminating from consideration at each stage those products that were thermodynamically favored but less likely to be formed from the kinetic standpoint. The general conclusions from the thermochemical analysis and the effects of temperature and the type of pesticide formulation on the equilibrium product distribution are discussed, in part, in the following sections.

4.1.3 Combustion of Pesticides

The distribution of the equilibrium products from the combustion of chlorinated hydrocarbon pesticide formulations depends on the temperature, the air/fuel ratio, and the carbon-hydrogen-chlorine-oxygen ratio in the original formulation. A brief summary of the primary equilibrium products and their relative concentrations as obtained from the thermochemical calculations is presented in Table 9.

Effects of Air/Fuel Ratio--

As indicated in Table 9, the product species O, NO, NO_2, ClO and HOCl are only found under excess air conditions, where as the product species CH_4, NH_3, and H are only found under oxygen deficient conditions. In addition, the formation of CO_2, Cl, Cl_2, H_2O, O_2, and OH is favored at higher air/fuel ratios, and the formation of CO and H_2 is favored at lower air/fuel ratios.

Effects of Temperature--

The effects of temperature on the relative concentrations of the equilibrium product species are illustrated in Figure 16 for the case of combustion of the 12 percent lindane emulsifiable concentrate with 30 percent excess air. In general, the formation of CO, Cl, ClO, NO, NO_2, H, and OH is favored by increasing the reaction temperature, whereas the formation of CH_4, CO_2, Cl_2, and NH_3 is favored by decreasing the reaction temperature. Increasing the reaction temperature also favors the formation of H_2 under stoichiometric or excess air conditions, and the formation of H_2O under oxygen deficient conditions. In addition, analyses of the results of the thermochemical calculations led to the following specific conclusions:

- Thermochemical analysis predicts that HCL formation is highly favored at pesticide incineration temperatures (1100 to 1650 K range), and that Cl_2, ClO and HOCl are found in only trace quantities. Cl is found in concentrations above 100 ppm at the higher incineration temperatures, but should react readily with the OH radical to form HCl and O_2 at lower temperatures. On the other hand, although the equilibrium concentration of Cl_2 increases to as much as 5000 ppm at the lower temperatures for the highly chlorinated pesticide formulations, the relative slowness of the reaction:

$$2HCl + 0.5O_2 \rightleftarrows H_2O + Cl_2$$

TABLE 9. EQUILIBRIUM PRODUCT DISTRIBUTION FROM THE COMBUSTION OF PESTICIDE FORMULATIONS

Case 1: Combustion with stoichiometric amount of air	
Major equilibrium products:	CO_2, H_2O, HCl, N_2.
Minor equilibrium products:	CO (< 1 to 460 ppm), H_2 (< 1 to 108 ppm), NO (< 1 to 71 ppm), Cl (< 1 to 391 ppm), Cl_2 (< 8 ppm), O_2 (< 1 to 180 ppm), OH (< 1 to 47 ppm).
Case 2: Combustion with 130% of stoichiometric air	
Major equilibrium products:	CO_2, H_2O, HCl, N_2, O_2.
Minor equilibrium products:	NO (1 to 1150 ppm), CO (< 1 to 21 ppm), NO_2 (< 2 ppm), O (< 6 ppm), OH (< 1 to 165 ppm), Cl (< 1 to 1433 ppm), Cl_2 (< 1 to 5073 ppm), ClO (< 7 ppm), HOCl (< 1 to 12 ppm), H_2 (< 6 ppm)
Case 3: Combustion with 70% of stoichiometric air	
Major equilibrium products:	CO, CO_2, H_2, H_2O, HCl, N_2
Minor equilibrium products:	CH_4 (< 1 to 8500 ppm), OH (< 2 ppm), NH_3 (< 1 to 55 ppm), Cl (< 1 to 25 ppm), H (< 1 to 20 ppm)

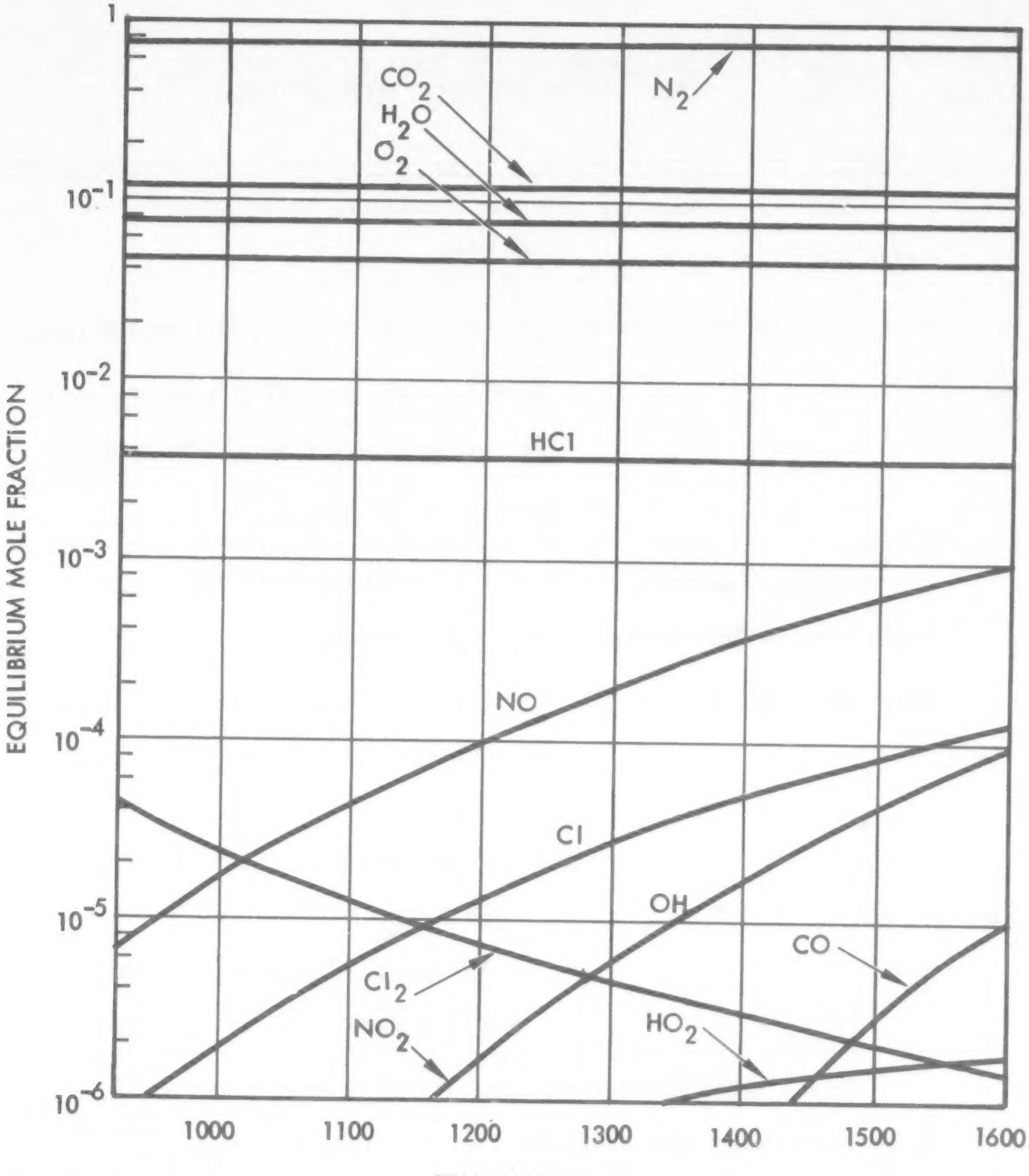

Figure 16. Equilibrium mole fraction of product species as a function of temperature from the combustion of 12 percent lindane emulsifiable concentrate with 30 percent excess air.

means that the reaction products will not have sufficient time to equilibrate, and that under actual incineration conditions HCl will still be the only predominant chlorinated compound found in the combustion products. Analyses of the grab samples taken during pesticide incineration tests confirmed that HCL was the only major chlorinated species found in the combustion products.

- CO formation increases with increasing reaction temperatures. At lower temperatures, the water-gas shift reaction:

  $$H_2O + CO \rightleftarrows H_2 + CO_2$$

  becomes the principal mechanism for equilibrating the amounts of CO and CO_2 present in the combustion products. To minimize the CO concentration in the incinerator effluent, the initial cooling of the incinerator gases should therefore be slow enough to allow for equilibration of all product species. The measured CO concentrations during pesticide incineration tests were found to be considerably higher than the corresponding calculated equilibrium CO concentrations, indicating that equilibrium for the water-gas shift reaction was not attained under test conditions.* From the equilibrium point of view, the concentrations of almost all the undesirable combustion products (with the exception of Cl_2) such as NO, NO_2, Cl, ClO, and CO, increase with increasing reaction temperature. Pesticide incineration should therefore be conducted at temperatures sufficiently high to cause complete combustion, and yet not excessively high as to lead to unacceptably large amounts of nitrogen oxides and carbon monoxide in the incinerator effluent.

Effects of Types of Pesticide Formulations--

The principal effects of different types of pesticide formulation on the equilibrium product distribution are the relative amounts of chlorinated species formed, which depend primarily on the Cl/C mole ratio of the formulation combusted. For example, the equilibrium concentrations of ClO and HOCl are found to be less than 1 ppm at Cl/C mole ratios of less than 0.0318 (corresponding to the mixture of 2,4-D ester, 2,4,5-T ester, and No. 2 fuel oil). The effects of Cl/C mole ratio on the equilibrium HCl and Cl_2 concentrations are presented in Figures 17 and 18, respectively, and indicate that the highly chlorinated pesticide formulations (such as the 72 percent chlordane emulsifiable concentrate and the 2,4,5-T ester) should be diluted with a fuel oil prior to incineration to minimize potential HCl corrosion and to safeguard against Cl_2 formation.

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*The oxidation of CO is discussed in greater detail in Section 4.1.4.

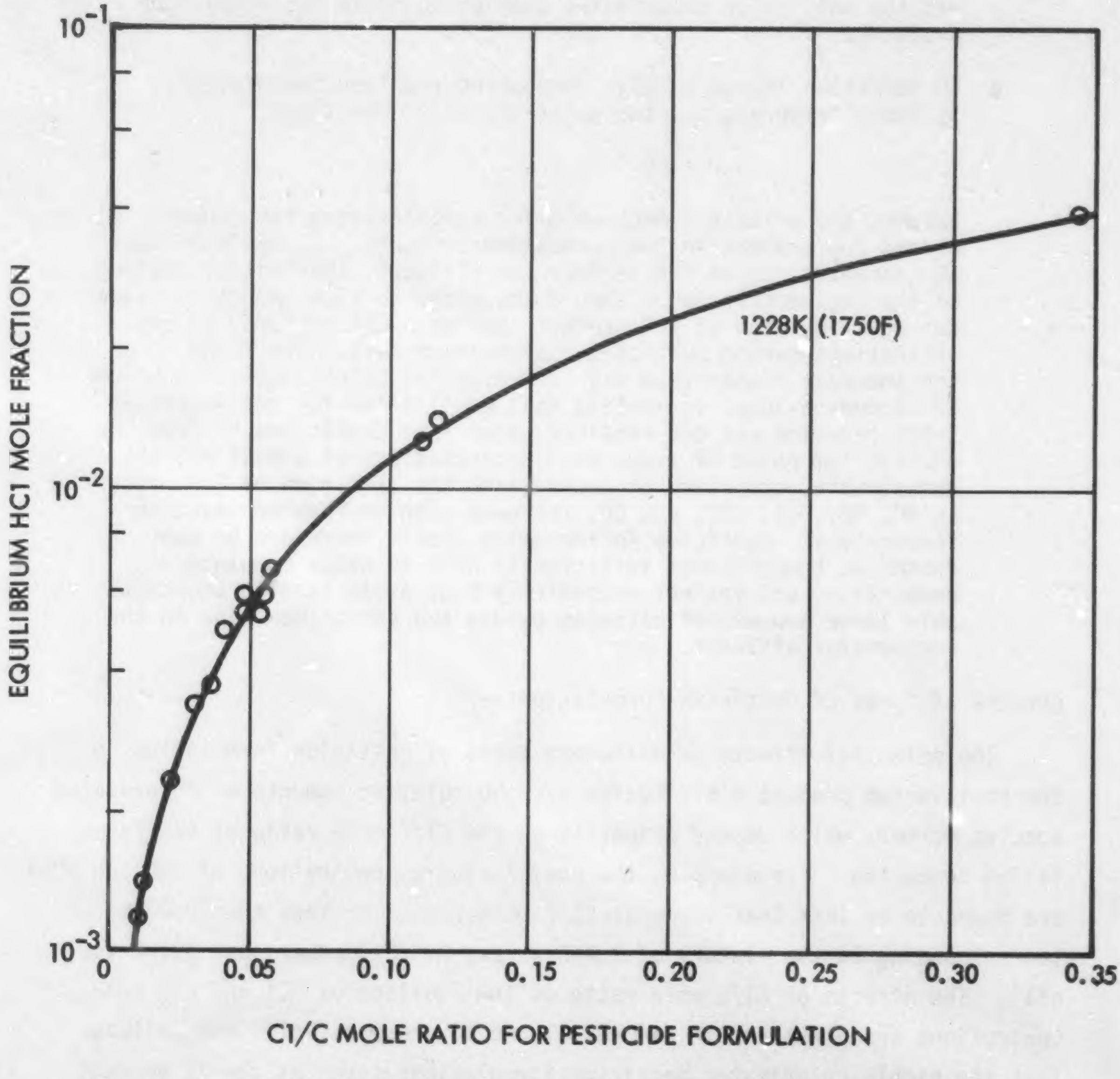

Figure 17. Equilibrium HCl concentration in combustion product gas resulting from the incineration with 30 percent excess air.

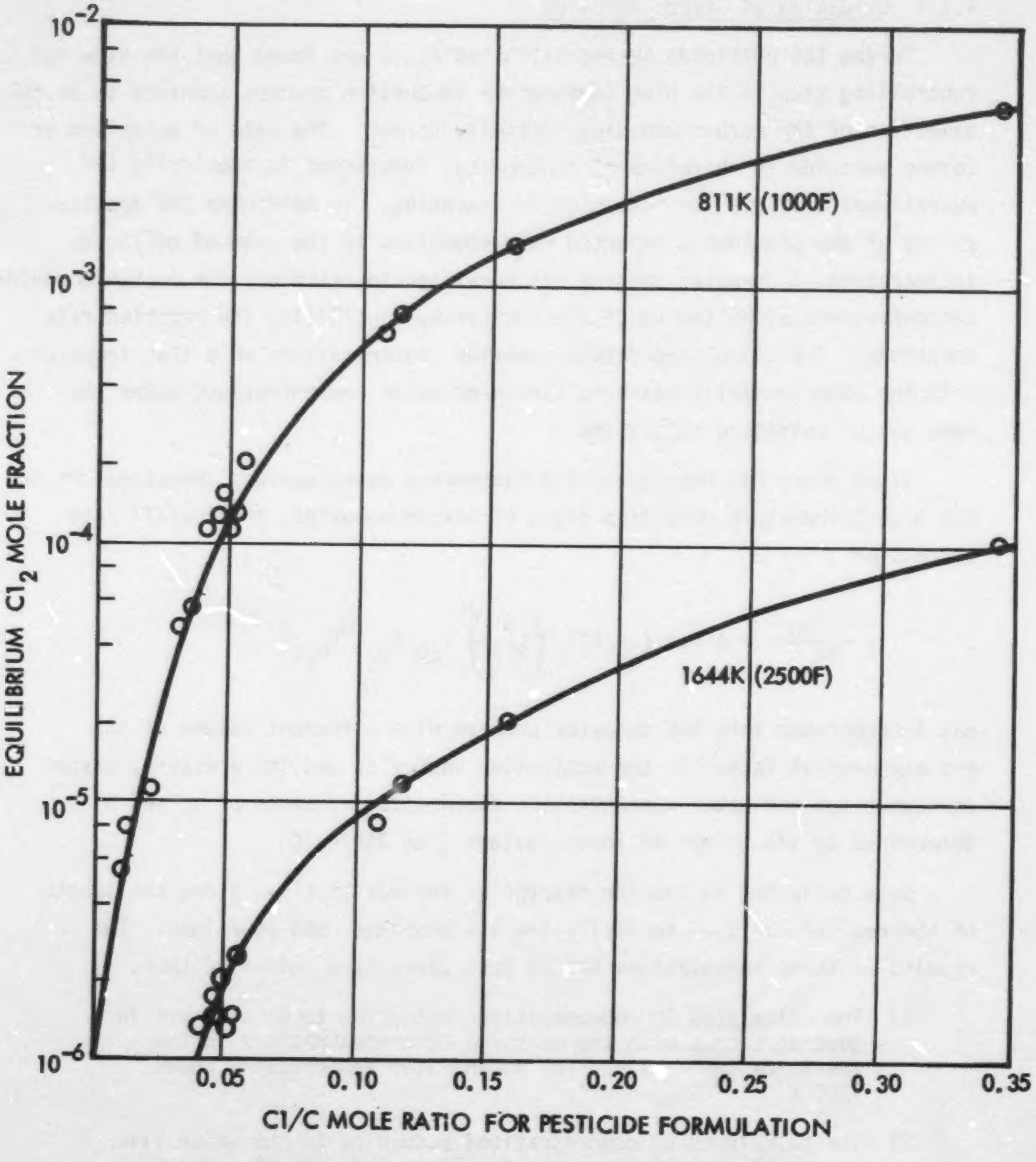

Figure 18. Equilibrium Cl_2 concentration in combustion product gas resulting from the incineration pesticide with 30 percent excess air.

4.1.4 Oxidation of Carbon Monoxide

During the pesticide incineration tests, it was found that the slow and controlling step in the high temperature combustion process appeared to be the oxidation of the carbon monoxide initially formed. The rate of oxidation of carbon monoxide is therefore of fundamental importance in specifying the operational criteria for pesticide incineration. To determine the applicability of the previously reported rate equations in the case of pesticide incineration, a computer program was developed to calculate the carbon monoxide concentrations along the pesticide incinerator, utilizing the reported rate equations. The calculated carbon monoxide concentrations were then compared with the experimentally measured carbon monoxide concentrations under the same set of operating conditions.

Since there has been general disagreement among various investigators on the high-temperature oxidation rates of carbon monoxide, the overall rate expression

$$-\frac{d\,C_{CO}}{dt} = A \exp(-E/RT) \left(\frac{P}{R'T}\right)^{p} f_{CO}\, f_{O_2}{}^{m} f_{H_2O}{}^{n}$$

was incorporated into the computer program with different values of the pre-exponential factor A, the activation energy E, and the pressure, oxygen concentration and water concentration dependence exponents p, m, and n as determined by six groups of investigators (see Table 10).

Data collected in tubular reactor at various stations along the length of the reactor was used to verify the six proposed rate equations. The results of these computations for 25 test cases have indicated that:

1) The calculated CO concentrations according to Sobolev are in good agreement with the measured CO concentrations in the pesticide incinerator, for incinerator temperatures above 1200 K.

2) The calculated CO concentrations according to the other five groups of investigators are far lower than the measured CO concentrations in the pesticide incinerator.

This conclusion is not too surprising as the Sobolev rate expression is the only one derived from direct measurements of the rate of oxidation of CO

TABLE 10. HIGH-TEMPERATURE OXIDATION RATES OF CARBON MONOXIDE

$$-\frac{d\,C_{CO}}{dt} = A \exp\,(-E/RT)\,\left(\frac{P}{R'T}\right)^{p} f_{CO}\, f_{O_2}{}^{m} f_{H_2O}{}^{n}$$

Investigator	Applicable f_{O_2}	$A \left(\frac{\text{liter}}{\text{mole}}\right)^{p-1} \frac{1^*}{\text{sec}}$	E cal/mole**	p	m	n
Fenimore and Jones	0 to 1.0	1.2×10^{9}	24000	2	1	0
Williams, et al.	0 to 1.0	1.8×10^{10}	25000	2	0.5	0.5
Hottel, et al.	0 to 1.0	1.2×10^{11}	16000	1.8	0.3	0.5
Friedman and Nugent	0 to 1.0	1.85×10^{7}	20000	1.5	0	0.5
Sobolev	0.05	6.44×10^{8}	27000	2	1	0
	0.05	5.86×10^{7}	27000	2.0	0.2	0
Kozlov	0.05	1.90×10^{13}	32000	2.5	1	0.5
	0.05	2.01×10^{12}	32000	2.5	0.25	0.5

*1 liter = 10^{-3} m^3

**1 calorie/mole = 4.19 joule/mole

in the afterburning zone instead of the flame front. The rate constants of the carbon monoxide reaction taking place in the flame front are generally several orders of magnitude larger than the rate constant of the chemical reaction taking place in the afterburning zone. However, at incinerator temperatures below 1200 K the Sobolev rate equation predicted a much slower carbon monoxide oxidation rate than that measured experimentally. As illustrated in Figure 19, the CO concentrations from both experimental measurements and determined by the Sobolev rate equation are considerably higher than the equilibrium CO concentration.

4.2 THE ROLE OF THERMOCHEMICAL EQUILIBRIUM ANALYSIS IN WASTE-INCINERATOR MATCHING

The number and quantities of chemical wastes are increasing, their disposal in bodies of water or in landfills is becoming less and less acceptable. As a consequence, clean-stack incineration will have to accommodate a fast growing list of chemical compounds. Selection of an incineration system capable of insuring complete and safe destruction can be aided by further developing the methodology which was used on chlorinated hydrocarbons and described in this section. The approach to selecting the means for the complete destruction hazardous species would include the following steps:

- Obtain the chemical composition and proportions of the waste.
- Determine the equilibrium composition of the products of combustion in oxygen rich and oxygen deficient mixtures in wide range of temperatures using the previously discussed computer model.
- Examine the initial equilibrium products distribution and determine those products that are not kinetically favored.
- In the next stage of calculations, determine another equilibrium product distribution by eliminating from consideration those products that are thermodynamically favored but less likely to be formed from the kinetic standpoint.
- Reiterate the above two steps
- Examine all of the above equilibrium products distributions to determine which initial compounds and possible intermediate species should be subjected to a laboratory test series (UDRI).

For many compounds laboratory tests will not be needed because the necessary conditions to achieve thermal decomposition and oxidation of

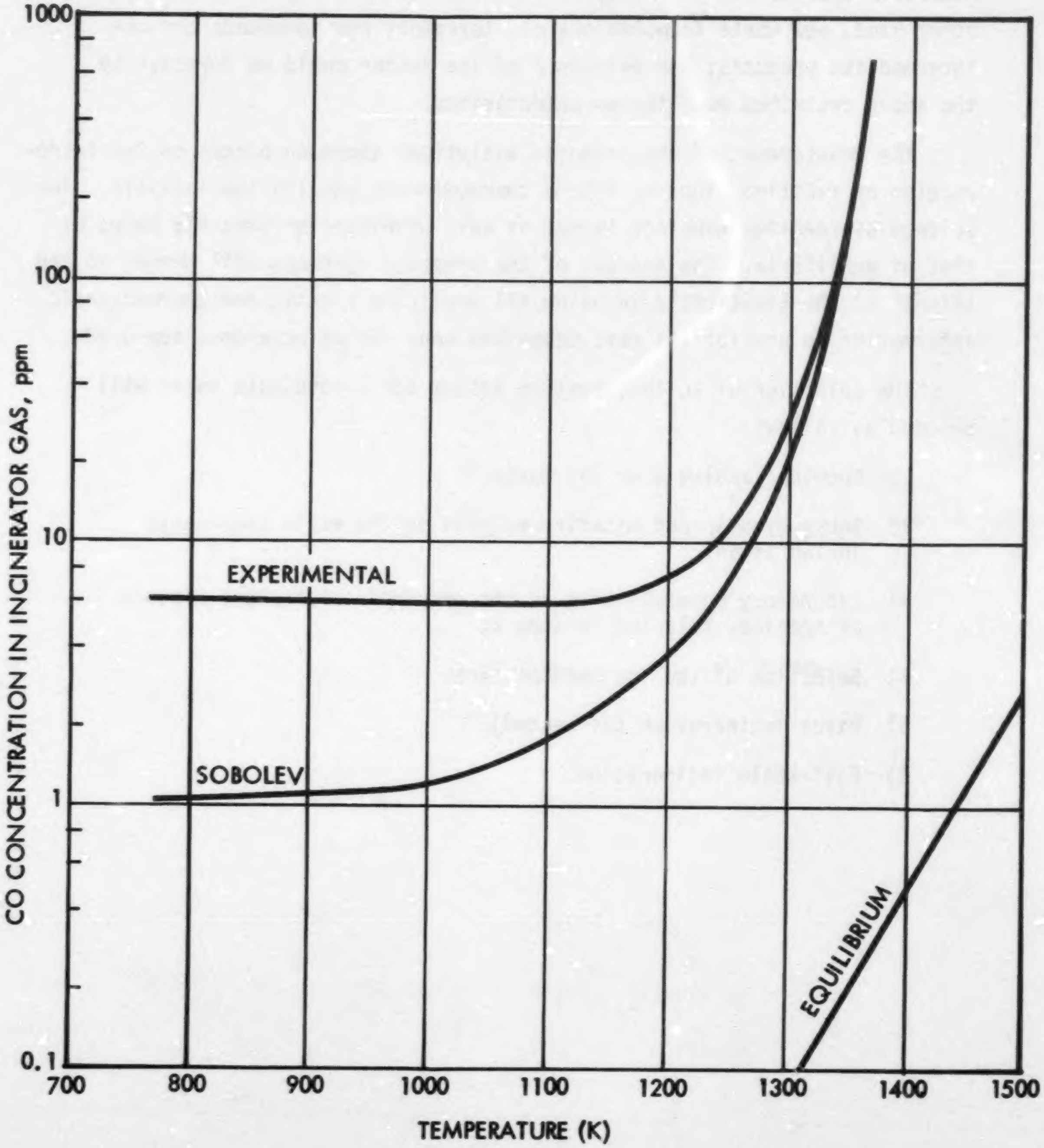

Figure 19. Comparison of experimental, kinetically determined, and equilibrium values of CO concentrations in the incinerator gas.

hazardous species can be safely established from prior experience. On the other hand, new waste formulations may introduce new compounds and new intermediate products; the existance of the latter could be forecast by the above described equilibrium computations.

The development of the proposed analytical approach hinges on the introduction of reaction kinetics into a thermodynamic equilibrium analysis. The science of reaction kinetics is not as well developed or securely based as that of equilibria. The success of the proposed appraoch will depend on the talents of the kineticists in using all available kinetic and thermodynamic information to predict the rate-dependent behavior of hazardous compounds.

The selection of an incineration system for a candidate waste will proceed as follows:

1) Chemical analysis of the waste.

2) Thermodynamic and kinetic analysis on the waste components incineration.

3) Laboratory determination of the required temperature history of species, selected in step 2.

4) Selection of the incinerator type.

5) Pilot incineration (if needed).

6) Full-scale incineration.

SECTION 5

SUMMARY AND RECOMMENDATIONS

Hazardous waste incineration in large commercial facilities is of growing importance because of the increasing volume of chemical wastes that must be safely destroyed. The study reported herein started with the selection of four incinerator types, based on their applicability to the largest volume and variety of wastes, and proceeded to identify the available experimental and analytical methods which could be used to predict the waste destruction efficiency and facilitate the scale-up of each incinerator type. Previous TRW studies and the open literature surveyed showed that neither the accurate prediction of waste incineration efficiencies, nor the establishment of adequate scale-up methods was possible today. Analytical methods and experimental correlations describing some of the important combustion and heat and mass-transfer mechanisms are available.

Analysis and modeling of incinerators have been most widely applied to liquid and fluidized bed incinerators; the work was not specifically directed towards, but is to a large degree applicable to, hazardous waste destruction. The continuing development of analytical methods and increasing volume of data pertaining to fluidized beds and liquid injection furnaces should be followed and exploited for that purpose. Not much analytical work or evidence of data collection was found for the rotary kiln or multiple hearth incinerators, so that the expectations of finding ongoing analytical work for these devices are unrealistic.

The mathematical modeling of rotary kilns does not appear to present unsurmountable difficulties. Still, some very basic information on the behavior of the solid charge and heat transfer between charge and kiln walls and charge and combustion gases is lacking. The multiple hearth incinerator is the device least amenable to analysis, hence in this case prediction will have to rely heavily on the acquisition of data, and on purely empirical correlations, at least in the near future.

The sheer size of the waste disposal problem warrants development of methodology for hazardous waste incineration. While the many gaps in the available information do not permit detailed modeling of incinerators, the pressing need to establish better design criteria and reduce the costs and risks involved in the testing of hazardous waste incinerators, a program to develop scale-up offers promise of success. For example, while the detailed equations governing the behavior of an incineration system are complex and often poorly understood, techniques such as dimensional analysis can be used to identify key parameters which govern the similarity of the various mechanisms of the destruction of hazardous waste components.

The term "similarity" needs to be qualified in order to be useful. We know that similarity of fluid flow in two geometrically similar systems is achieved if the Reynolds numbers are the same in both systems, assuming that the fluid is incompressible and gravitational forces small. If these assumptions do not apply, the Mach number and Froude numbers must also be replicated (45). It has also been shown that to achieve a similarity in convective heat flux between a flowing fluid and a surface the Nusselt number must be reproduced. The relationship $Nu = f(Re, Pr)$ can be derived through dimensional analysis or by examination of the Navier Stokes and the energy equations (45, p 253). In the case of incineration of hazardous waste, the similarity should be viewed in light of the objective of the incinerator. A potential definition of similarity is as follows:

> Two geometrically similar incinerators of different capacity are deemed similar if, when burning the same type of waste, they produce the same level of destruction and their stack gases and residues respectively have the same composition.

Since incinerators will be handling wide varieties of wastes it is not possible to use emission levels directly. However, the degree of waste decomposition or oxidation depends almost entirely on the three T's of incineration: time, temperature and turbulence. The alliteration is somewhat misleading, as turbulence mostly stands for mixing and dispersion (e.g., exposing fuel to oxidizer, and contact between solids and gases) and time refers to residence time of a reactant or fuel above a specified temperature level. It appears, from previous research, that if two geometrically similar devices have identical residence times at specified temperature levels and provide for equal levels of mixing at those temperatures, the same level of waste destruction (through thermal decomposition and oxidation) will be achieved. A research program can be directed to determine which dimensonless parameters need to be taken into account in order to insure incinerator similarity. For example, in a rotary kiln similarity may require equivalent Reynolds, Biot and Nusselt numbers in different zones of the kiln. Because of material restrictions and because of contradictory demands that may be presented by each mechanism (e.g., high velocity for equivalent mixing vs low velocity for equivalent residence time) full similarity may not be achieved. Analytical and experimental work will be needed to determine which parameters influence similarity of emissions most.

We recommend that the following tasks be included in the development of a hazardous waste incineration program:

- Continue the thermal decomposition experiments of hazardous components of waste.
- Initiate similar experiments on decomposition in the presence of oxygen.
- Canvass the major manufacturers of incinerators, furnaces and fluidized beds to determine the extent and applicability of in-house and government funded development programs.
- Collect existing data on gas composition CO, O_2, unburned hydrocarbons etc., upstream of pollution control equipment, and data on the effectiveness of control equipment installed on incinerators.
- Develop plan and recommendations for instrumentation installations on commercial incinerator and for data gathering.
- Develop an analytical model for rotary kiln incineration. (Imber and Paschke's paper is a good starting point.)

- Initiate the development of analysis using a statistics approach, leading to the evaluation of the probability of emissions exceeding preimposed levels. A statistical approach is appropriate since the waste decomposition and oxidation take place in a distribution of temperature and residence time, and mixing is not uniform.

- Investigate a systematic approach to combining furnace models (for example by the zone method) with experimental results to build predictive analytical tools.

The development of a waste incineration methodology is by its very nature a continuing effort as the composition of the wastes will certainly change with time.

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